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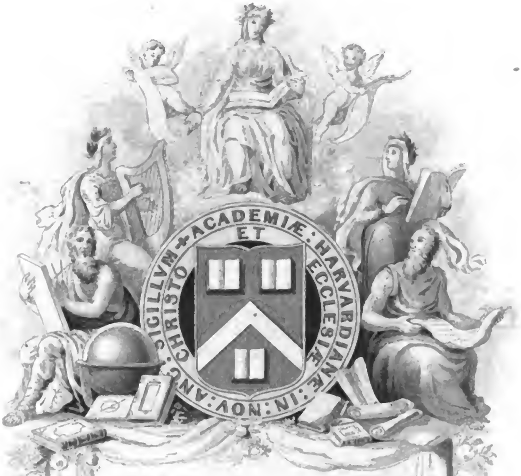
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THE

QUARTERLY JOURNAL

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Nov. 20, 1848.

William Allen Miller, M.D., in the Chair.

The following presents were laid on the table:—"An Essay on the comparative value of different kinds of Coal for the purposes of illumination," by A. Fyfe, M.D., presented by the author, and Taylor's Calendar of the Meetings of Scientific Bodies for 1848-49, also from the author. Messrs. Alexander Bain and William John Hay, were duly elected members of the Society.

The following letter and communications were read:

On traces of Copper and Lead in the ashes of Coal, by J. ARTHUR PHILLIPS, ESQ., *in a Letter to Mr. Warington.*—The writer having read with much interest a paper by Mr. Vaux, in the Transactions of the Society, in which was a list of coals containing traces of copper and lead recorded, was induced to repeat the experiments on the ashes of some of the coals, which had passed through his hands in connexion with "the Admiralty Coals Investigation;" in no instance however was he able to detect the presence of the slightest trace of either of those metals.

Mr. Phillips' experiments were made on the ashes of the following coals from Newcastle, viz.:

Carr's Hartley, Newcastle Hartley, and
North Percy Hartley;

these were followed by the examination of some specimens from Liverpool, viz:

The Laffak Rushy Park.
The Johnson's and Worthington's, Sir John, and
The Blackbrook Rushy Park.

Wigan Coals.

The Balcaries Lindsay.

Scotch Coals.

The Eglington, The Wellwood,
The Fordel Splint, and Wallsend Elgin.

Welsh Coals.

The Pontypool, The Bedwas,
The Porthmawr, The Ebbw Vale, and
Linoi Coals.

An anthracite from Slievardagh in Ireland, and a specimen of coal from Conception Bay, Chili, were also tried with the same results.

It would therefore appear, that although traces of copper and lead may occasionally occur in coal, their presence is extremely rare in the districts above mentioned.

In these experiments care was taken to employ water perfectly free from metallic salts, as on examining the ordinary distilled water of the laboratory, some of it was found to darken slightly on passing a current of sulphuretted hydrogen through it; no water was, therefore, employed which had not been previously tested and ascertained to be free from traces of the metals.

Analysis of Black-ash, Soda-ash, &c., by FREDERIC MUSPRATT, ESQ. —Conducting the operations in an extensive Soda Manufactory, I have repeatedly to investigate the several processes in all their intricate relations, and more especially to analyse the numerous products in order to arrive at the *necessary* quantities of the different substances that should be employed in the mixtures, for the production of a black-ash that would yield, when lixiviated, the largest amount of subcarbonate of soda. In the fabrication of soda, as in all other technological processes, correct data can only be arrived at by ascertaining exactly the composition of the products. Some of my results are completed, and as they may prove interesting to the Society, I transmit them through my brother, Dr. Muspratt. The analysis of black-ash being somewhat complex, my mode of procedure is appended, as it may facilitate the progress of others embarking in a similar field of research.

I dissolved a weighed portion of black-ash in aqua regia, boiled and filtered the solution.

1. The residue was weighed on a dried filter. It consisted of charcoal and sand.

2. I evaporated the filtrate, and digested the residue with hydrochloric acid; filtered again, and determined the amount of silica which remained.

3. The solution was treated with ammonia, to precipitate the phosphate of lime and peroxide of iron, which were ignited and weighed.

4. I treated the filtrate from 3 with oxalate of ammonia, precipitating the lime, from the amount of which I calculated its compounds with sulphur and carbonic acid.

5. The filtrate was evaporated with sulphuric acid, to obtain sulphate of soda and sulphate of magnesia, from which, after deducting the magnesia, determined in the usual manner by dissolving the compound and precipitating with phosphate of soda and ammonia, I obtained the soda; and after calculating the quantity that existed in combination, determined the amount of caustic soda.

Another portion of the ash was treated with concentrated nitric acid, and the sulphuric acid precipitated by means of nitrate of baryta.

Water was then added to another weighed quantity of black-ash, till all the soluble portion was dissolved. The solution was then measured into three parts, and the chloride of sodium, sulphate of soda, and sulphide of sodium were respectively determined.

The amount of carbonic acid was ascertained with the aid of Will's apparatus; an aqueous solution gave, in the first instance, the carbonic acid combined with soda, and secondly, the black-ash treated with an excess of chromate of potash yielded the total quantity of carbonic acid.

ANALYSIS OF BLACK-ASH.

		Calculated on 100 parts without charcoal and sand.
Carbonate of soda . .	17·181	18·804
Caustic soda* . . .	7·970	8·723
Sulphate of soda . .	1·500	1·642
Sulphide of sodium . .	0·900	0·985
Chloride of sodium . .	2·600	2·846
Sulphide of calcium . .	26·048	28·509
Carbonate of lime . .	17·045	18·655
Caustic lime . . .	8·355	9·144
Peroxide of iron . . . Phosphate of lime . .	3·817	4·178
Silicate of magnesia . .	1·480	1·620
Silicate of soda . .	4·472	4·894
Charcoal and sand . .	7·942	—
	99·280	100·000

---

* Since this analysis was read to the Society, a paper on the products of the Soda Manufacture, by Mr. John Brown, has appeared in the Philosophical Magazine for January 1849, in which the author objects to the manner in which Unger and Richardson have stated their results with regard to the carbonate and caustic soda. Their determinations appear to me most satisfactory, as they represent the value of the compound obtained in the process of manufacture in the same way that one would state the richness of a metal procured in the manufacture of prussiate of potash. Did the

The above results justify the assumption that a double salt of sulphide of calcium and lime is formed, which is insoluble in water, whereas the sulphide of calcium is soluble.

The method employed in analysing soda-ash, was similar to that described with reference to black-ash, it will therefore be unnecessary to repeat it.

ANALYSIS OF SODA-ASH.

		Calculated on 100 parts without charcoal and sand.
Carbonate of soda . .	77·085	78·428
Caustic soda . . .	4·881	4·961
Sulphate of soda . .	5·110	5·198
Sulphide of sodium . .	0·630	0·640
Carbonate of lime . .	0·320	0·325
Peroxide of iron . .	0·324	0·329
Carbonate of potash . .	0·200	0·204
Cyanide of sodium . .	0·012	0·013
Silicate of soda . . .	2·400	2·442
Chloride of sodium . .	7·130	7·256
Sulphide of calcium . .	0·200	0·204
Charcoal and sand . .	0.659	—
	98·951	100·000

It will be seen from the above analysis, that the quantity of caustic soda is very small, proving that the carbonates generally employed may be dispensed with, as the access of air performs their office sufficiently for general purposes.

I have also had occasion to examine many specimens of pyrites, both before and after ignition, and have invariably found the burnt pyrites to contain its sulphur in the form of sulphuric acid, most probably in the state of a basic salt. The mass is perfectly insoluble in water.

I.—*Analyses of the Ashes of some Esculent Vegetables.*

By Thornton John Herapath, Esq.

At a period when so much attention is paid by scientific men, both at home and abroad, to the inorganic constituents of plants, and when many of our chemists of the first standing are engaged in their analysis, the detail of the results of some experimental

quantity of caustic soda depend *entirely* on the excess of lime employed, the carbonate and caustic soda might be readily calculated, as well as the compound salt of the sulphide of calcium.

inquiries, which I have lately instituted, into the chemical constitution of the ashes of some of our commonest esculent vegetables, though few in number, may not be thought uninteresting by the members of the Society; for although my recent experiments on this subject, which I have already had the honour of communicating to the Society, would appear to show that we must not expect much benefit to result to physiology from the analysis of the inorganic substances contained in such a heterogeneous assemblage of parts as that which occurs in any separate organ of a plant, still it cannot but be admitted by every chemist who may have witnessed the great improvements which have, of late years, been introduced in the cultivation of the soil, that such analyses have proved, and are still proving, of the greatest assistance to the practical agriculturist in numerous ways, and are of especial service in pointing out to him those particular substances which are most beneficial as manures for his crops. It was with this latter object in view that the following analyses were undertaken.

All the specimens examined were particularly fine and in excellent preservation, and were, with very few exceptions, obtained from the places in which they were growing, by myself; I was consequently enabled to ascertain every circumstance connected with their growth which it was necessary for me to be acquainted with.

The greatest care was taken to remove all extraneous matters from the plant prior to burning.

The processes followed in the preparation and analysis of the ashes have been already described in a former paper to the Society.

I.—SCURVY-GRASS (*Cochlearia anglica*).

This vegetable, as is well known, although not ordinarily considered as an article of food, is occasionally resorted to as such by sailors, after returning from long voyages, or when suffering from scurvy, produced by a deficiency of vegetable aliment. It has been found particularly beneficial to persons suffering under this disease, and hence is derived its popular name.

The plants, the ashes of which were submitted to examination, were found growing on the *débris* of new red sandstone-rocks, near the banks of the river Avon, which were occasionally submerged at high tide.

a. 6440 grs. of the fresh specimen (entire), gave 740 grs. of dry vegetable matter, which left upon incineration 156 grs. of ash.

b. 5000·00 grs. of fresh, gave 574·70 grs. of dry, plant, which left 121·11 grs. of ash.

These experiments give 2·4222 as the mean per-centage of ash from the fresh, and 21·0770 as that from the dry, plant.

These ashes were found to consist in 100 parts of:

	I.	II.	MEAN.
SOLUBLE SALTS:			
Carbonic acid	3·580	3·560	3·570
Sulphuric acid	3·024	3·244	3·134
Phosphoric acid	traces.	traces.	traces.
Potash	traces.	0·100	0·050
Soda	7·710	7·764	7·737
Chloride of sodium	63·510	63·758	63·634
INSOLUBLE SALTS:			
Carbonate of lime	7·079	7·279	7·179
,, ,, magnesia	1·093	1·471	1·282
Sulphate of lime	traces.	traces.	traces.
Phosphate of lime (*tribasic*)	11·030	9·482	10·256
,, ,, magnesia	traces.	traces.	traces.
Perphosphate of iron	0·503	0·779	0·641
Silicic acid	2·495	2·633	2·564
	100·024	100·070	100·047

Deducting the carbonic acid, we obtain the following per-centage composition:

Sulphuric acid	3·383
Phosphoric acid	5·433
Potash	0·054
Soda	8·359
Chloride of sodium	68·701
Lime	10·282
Magnesia	0·658
Sesqui-oxide of iron	0·367
Silicic acid	2·763
	100·000

II.—CELERY (*Apium graveolens*).

a. 1555·0 grs. of the fresh young shoots gave 101·4 grs. of dry vegetable matter, and left 17·1 grs. of ash upon incineration.

b. 4546·70 grs. of the same specimen gave 307·25 grs. of dry matter, and 50·00 grs. of ash.

Mean per-centage of ash	from the fresh plant	1·0996
	,, ,, dried ,,	16·2720

	I.	II.	MEAN.
Soluble salts:			
Carbonic acid	7·967	8·407	8·187
Sulphuric acid	0·957	0·983	0·970
Phosphoric acid	6·419	6·423	6·421
Potash	29·019	29·657	29·338
Soda	traces.	traces.	traces.
Chloride of sodium	32·909	31·651	32·280
Insoluble salts:			
Carbonate of lime	7·310	7·652	7·481
„ „ magnesia	traces.	traces.	traces.
Sulphate of lime	„	„	„
Phosphate of lime (*tribasic*)	13·091	14·279	13 685
„ „ magnesia	—	—	—
Perphosphate of iron	traces.	traces.	traces.
Silicic acid	2·092	1·182	1·637
	99·764	100·234	99·999

After the deduction of the carbonic acid, the composition in 100 parts will be:

Sulphuric acid	1·095
Phosphoric acid	14·390
Potash	33·144
Soda	traces.
Chloride of sodium	36·466
Lime	13·056
Magnesia	traces.
Sesquioxide of iron	„
Silicic acid	1·849
	100·000

III.—SEA-KALE (*Crambe maritima*).

I have analysed the ashes of this plant, taken at two different periods of its growth; firstly, those of the full-grown leaf and petiole; and, secondly, those of the young blanched sprouts; the plant, in the meantime, having been well manured with horse-dung.

Soil.—Rich, porous, and sandy garden ground, lying on the millstone-grit, which contained a pretty large proportion of carbonate of lime.

a. 1097·0 grs. of the fresh leaf, &c., gave 113·4 grs. of dry vegetable matter, and left 19·0 grs. of ash upon incineration.

b. 1737·0 grs. of the same specimen, gave 179·0 grs. of dry matter, and 30·004 grs. of ash.

Mean per-centage of ash	from the fresh leaf, &c. .	1·732
	,, ,, dried ,, ,, .	16·736

a. 1158·0 grs. of the fresh young sprouts gave 83·4 grs. of dry vegetable matter, and left, upon incineration, 8·298 grs. of ash.

b. 1737·0 grs. of the same specimens gave 125·1 grs. of dry matter, and 12·447 grs. of ash.

Mean per-centage of ash	from the fresh young sprouts.	0·7108
	,, ,, dried ,, ,,	9·9490

	Old plant. I.	Young plant. II.
Soluble salts:		
Carbonic acid	6·921	4·217
Sulphuric acid	15·157	21·848
Phosphoric acid	traces.	5·061
Potash	2·105	6·748
Soda	20·800	23·584
Chloride of sodium . . .	12·542	traces.
Insoluble salts:		
Carbonate of lime. . . .	27·168	3·615
,, ,, magnesia . . .	some	traces.
Sulphate of lime	1·515	traces.
Phosphate of lime (tribasic) . .	12·105	30·710
,, ,, magnesia. . .	traces.	traces.
Perphosphate of iron . . .	1·582	traces.
Silicic acid	0·105	4·217
	100·000	100·000

Carbonic acid being deducted, the following is the composition in 100 parts:

	I.	II.
Sulphuric acid	19·782	23·195
Phosphoric acid	7·998	19·926
Potash	2·594	7·164
Soda	25·640	25·039
Chloride of sodium . . .	15·465	traces.
Lime	27·557	20·199
Magnesia	traces.	traces.
Oxide of iron	0·835	traces.
Silicic acid	0·129	4·477
	100·000	100·000

IV.—ASPARAGUS (*Asparagus officinalis*).

The following are the analyses of two full-grown specimens of this vegetable. The first of these was taken from a piece of garden ground near Bristol, the soil of which was similar to that described under No. III, and the other was found growing wild, on alluvium, on the banks of the Avon, which was daily overflowed by the river. They were both gathered whilst in flower.

a. 285·9 grs. of the fresh cultivated plant gave 72·1 grs. of dry vegetable matter, which furnished upon incineration, 4·38 grs. of ash.

b. 714.7 grs. of the same specimen (fresh), gave 180·25 grs. of dry matter, and 10·951 grs. of ash.

Mean per-centage of ash	from the fresh plant .	1·5321
	„ „ dried „ .	6·0748

a. 486·2 grs. of the fresh wild plant gave 175·0 grs. of dry vegetable matter, and left 11·78 grs. of ash, upon incineration.

b. 1701·7 grs. of the same specimen (fresh), gave 612·5 grs. of dry matter, and 41·23 grs. of ash.

Mean per-centage of ash	from the fresh plant .	2·4220
	„ „ dried „ .	6·7304

	Cultivated plant.			Uncultivated plant.
SOLUBLE SALTS:	I.	II.	MEAN.	I.
Carbonic acid . .	14·636	13·902	14·269	4·861
Sulphuric acid . .	3·509	3·605	3·557	7·775
Phosphoric acid . .	2·181	2·019	2·100	traces.
Potash	32·695	32·783	32·739	15·815
Soda	—	—	—	2·719
Chloride of sodium. .	traces.	traces.	traces.	20·514
„ „ potassium .	13·103	13·015	13·059	—
INSOLUBLE SALTS:				
Carbonate of lime . .	14·511	14·711	14·611	21·432
„ „ magnesia .	—	—	—	2·617
Sulphate of lime . .	traces.	traces.	traces.	traces.
Phosphate of lime (tribasic)	16·197	16·223	16·210	21·670
„ „ magnesia .	traces.	traces.	traces.	traces.
Perphosphate of iron .	0·412	0·500	0·456	1·699
Silicic acid . . .	2·803	3·133	2·968	0·849
	100·047	99·891	99·969	99·951

Deducting the carbonic acid, the following is the composition in 100 parts:

	Cultivated plant.	Uncultivated plant.
Sulphuric acid	4·487	9·224
Phosphoric acid	12·357	12·812
Potash.	41·299	18·766
Soda	—	3·225
Chloride of sodium . . .	traces.	24·337
" " potassium . . .	16·473	—
Lime	21·332	28·081
Magnesia	—	1·479
Oxide of iron	0·308	1·069
Silicic acid	3·744	1·007
	100·000	100·000

I have likewise analysed the ashes of the young heads of asparagus; such as were in a fit state for the table.

The results of my analysis are as follows:

a. 1839·0 grs. of the fresh shoots gave 133·0 grs. of dry vegetable matter, which left, after incineration, 14·95 grs. of ash.

b. 4597·5 grs. of the same specimen (fresh), gave 332·0 grs. of dry matter, and 37·37 grs. of ash.

Mean per-centage of ash	from the fresh plant .	0·8129
	" " dried " .	11·2400

Soluble salts:	I.	II.	MEAN.
Carbonic acid. . . .	3·925	4·101	4·013
Sulphuric acid . . Phosphoric acid . .	31·199	30·967	31·083
Potash . . . . Soda	32·605	32·665	32·635
Chloride of sodium. . " " potassium .	10·090	10·030	10·060
Insoluble salts:			
Carbonate of lime . .	6·832	7·080	6·956
" " magnesia .	—	—	—
Sulphate of lime . .	traces.	traces.	traces.
Phosphate of lime (tribasic)	14·040	14·052	14·046
" " magnesia .	traces.	traces.	traces.
Perphosphate of iron .	0·209	0·203	0·206
Silicic acid	1·100	0·902	1·001
	100·000	100·000	100·000

Sulphuric and phosphoric acids . . .	40·530
Potash and soda	35·118
Chlorides of sodium and potassium . . .	10·825
Lime	12·331
Magnesia	traces.
Oxide of iron.	0·119
Silicic acid	1·077
	100·000

V.—CAULIFLOWER (*Brassica oleracea* var. ε *botrytis*).

The specimens examined of this plant, were brought from Cornwall, where they are cultivated in the greatest perfection.

Soil.—Somewhat loamy, very rich, and well manured.

a. 1800·0 grs. of the fresh plant (entire), gave 159·0 grs. of dry vegetable matter, and furnished, when incinerated, 14·0 grs. of ash.

b. 9500 grs. of the same specimen gave 796·0 grs. of dry matter, and 70·25 grs. of ash.

Mean per-centage of ash	from the fresh plant .	0·7585
	„ „ dried „ .	8·8151

	I.	II.	MEAN.
SOLUBLE SALTS:			
Carbonic acid. . .	3·914	3·914	3·914
Sulphuric acid . .	12·101	13·379	12·740
Phosphoric acid . .	6·749	6·731	6·740
Potash	20·932	21·296	21·114
Soda	6·009	5·961	5·985
Chloride of sodium . .	7·269	7·051	7·160
„ „ potassium .			
INSOLUBLE SALTS:			
Carbonate of lime . .	14·161	13·597	13·879
„ „ magnesia .	traces.	traces.	traces.
Sulphate of lime . .	traces.	traces.	traces.
Phosphate of lime (tribasic)	26·099	25·853	25·976
„ „ magnesia .	traces.	traces.	traces.
Perphosphate of iron .	1·112	1·018	1·065
Phosphate of alumina .	traces.	traces.	traces.
„ „ manganese .			
Silicic acid . . .	1·400	1·446	1·423
	99·746	100·246	99·996

The carbonic acid being deducted, the following is the composition of the ash in 100 parts:

Sulphuric acid	14·158
Phosphoric acid	22·135
Potash	23·463
Soda	6·651
Chloride of sodium	7·956
„ „ potassium	
Lime	23·333
Magnesia	traces.
Oxide of iron	0·723
Alumina.	traces.
Oxide of manganese.	
Silicic acid	1·581
	100·000

VI.—KIDNEY BEAN (*Phaseolus multiflorus*).

This vegetable, together with all those subsequently examined, grew on rich, well-manured and drained sandy soils, in the neighbourhood of Bristol, lying on the millstone grit, and new red sandstone, which contained considerable quantities of carbonate of lime, and red oxide of iron, with a very notable proportion of carbonate of magnesia.

a. 1284·0 grs. of the fresh young legumes gave 76·0 grs. of dry vegetable matter, and left 8·11 grs. of ash, upon incineration.

b. 1000·0 grs. of the same, gave 58·9 grs. of dry matter, and left 6·305 grs. of ash.

Mean per-centage of ash	from the fresh legumes.	0·6310
	„ „ dried „	10·6875

The ash contained:

Soluble salts:	
Carbonic acid	14·081
Sulphuric acid	3·378
Phosphoric acid	1·553
Potash	36·103
Soda	—
Chloride of sodium	4·932
Insoluble salts:	
Carbonate of lime	22·194
„ „ magnesia	3·822
Sulphate of lime	traces.
Phosphate of lime (tribasic)	11·866
„ „ magnesia	traces.
Perphosphate of iron	traces.
Silicic acid	2·071
	100·000

Or calculated after deducting carbonic acid.

Sulphuric acid	4·553
Phosphoric acid	9·451
Potash	48·667
Soda	—
Chloride of sodium	6·648
Lime	25·337
Magnesia	2·553
Oxide of iron	traces.
Silicic acid	2·791
	100·000

VII.—ONION (*Allium sativum*).

1597·0 grs. of the fresh root, when dried and incinerated, left 8·71 grs. of ash = 0·5453 per cent.

The ash contained :

SOLUBLE SALTS :	
Carbonic acid	12·169
Sulphuric acid	4·821
Phosphoric acid	2·181
Potash	35·132
Soda	some.
Chloride of sodium	2·755
INSOLUBLE SALTS :	
Carbonate of lime	5·740
„ „ magnesia	6·886
Sulphate of lime	none.
Phosphate of lime (tribasic)	30·089
„ „ magnesia	traces.
Perphosphate of iron	traces.
Silicic acid	0·224
	99·997

Or calculated after deducting carbonic acid.

Sulphuric acid	5·900
Phosphoric acid	19·668
Potash	43·001
Soda	some.
Chloride of sodium	3·372
Lime	23·765
Magnesia	4·014
Oxide of iron	traces.
Silicic acid	0·280
	100·000

VIII.—COMMON WHITE GARDEN-TURNIP (*Brassica rapa*).

a. 1830·0 grs. of the fresh roots, cut in thin slices, gave 160·0 grs. of dry vegetable matter, and left upon incineration 11·863 grs. of ash.

b. 1542·6 grs. of the same, gave 134·87 grs. of dry matter, and 9·998 grs. of ash.

Mean per-centage of ash	from the fresh roots	0·6481
	„ „ dried „	7·4136

The ash contained:

SOLUBLE SALTS:	
Carbonic acid	14·692
Sulphuric acid	2·141
Phosphoric acid	4·518
Potash	39·146
Soda	—
Chloride of sodium	11·936
INSOLUBLE SALTS:	
Carbonate of lime	3·287
„ „ magnesia	4·046
Sulphate of lime	traces.
Phosphate of lime (tribasic)	19·223
„ „ magnesia	traces.
Perphosphate of iron	traces.
Silicic acid	1·011
	100·000

Or calculated after deducting carbonic acid.

Sulphuric acid	2·619
Phosphoric acid	16·620
Potash	47·888
Soda	—
Chloride of sodium	14·601
Lime	14·679
Magnesia	2·357
Oxide of iron	traces.
Silicic acid	1·236
	100·000

IX.—SWEDE TURNIP, OR RUTA-BAGA (*Brassica campestris*, var. *napo-brassicæ*).

a. 2116·0 grs. of the fresh young roots gave 355·0 grs. of dry vegetable matter, and left 26·05 grs. of ash upon incineration.

b. 6348·0 grs. of the same gave 1065·0 grs. of dry matter, and 78·15 grs. of ash.

Mean per-centage of ash	from the fresh roots .	1·2311
	,, ,, dried ,, .	7·2817

The ash was composed of:

	I.	II.	MEAN.
SOLUBLE SALTS:			
Carbonic acid . . .	17·349	16·893	17·121
Sulphuric acid . .	3·196	3·534	3·365
Phosphoric acid . .	6·897	7·891	7·394
Potash	51·070	49·786	50·428
Soda	traces.	traces.	traces.
Chloride of sodium . . ,, ,, potassium .	5·890	5·994	5·942
INSOLUBLE SALTS:			
Carbonate of lime . .	2·289	2·322	2·305
,, ,, magnesia .	2·589	2·452	2·520
Sulphate of lime . .	traces.	traces.	traces.
Phosphate of lime (tribasic)	7·943	7·955	7·949
,, ,, magnesia .	2·487	2·191	2·339
,, ,, alumina . ,, ,, manganese .	traces.	traces.	traces.
Perphosphate of iron .	0·400	0·366	0·383
Silicic acid . . .	0·087	0·062	0·074
	100·197	99·446	99·820

Yielding the following quantities in 100 parts, after deducting the carbonic acid:

Sulphuric acid	4·242
Phosphoric acid	15·890
Potash	62·631
Soda	traces.
Chlorides of sodium and potassium .	7·439
Lime	6·922
Magnesia	2·531
Alumina and oxide of manganese .	traces.
Oxide of iron	0·251
Silicic acid	0·094
	100·000

X.—Beet (*Beta vulgaris*).

a.—1950·0 grs. of the sliced roots of the variety called the "Long Red," when dried and incinerated, 'gave 19·22 grs. of ash = 0·9856 per cent.

Composition of the ash:

Soluble salts:	
Carbonic acid	17·876
Sulphuric acid	6·082
Phosphoric acid	traces.
Potash	39·016
Soda	
Chloride of sodium	5·962
Insoluble salts:	
Carbonate of lime	15·609
Carbonate of magnesia	4·162
Sulphate of lime	traces.
Phosphate of lime (tribasic)	11.293
,, ,, magnesia	traces of each.
,, ,, alumina	
Perphosphate of iron	
Phosphate of manganese	
Silicic acid	
	100·000

The composition calculated on 100 parts, after deducting the carbonic acid, was:

Sulphuric acid	8·322
Phosphoric acid	7·101
Potash	53·463
Soda	
Chloride of sodium	8·158
Lime	20·244
Magnesia	2·712
Alumina	traces of each.
Oxide of iron	
,, ,, manganese	
Silicic acid	
	100·000

XI.—Radish (*Raphanus sativus*).

a.—875·0 grs. of the fresh root gave 35·218 grs. of dry vegetable matter, and left 7·25 grs. of ash upon incineration.

b.—6000·0 grs. of the same specimen gave 242·08 grs. of dry matter, and 49·8 grs. of ash.

Mean per-centage of ash	from the fresh roots	0·8285
	„ „ dried „	20·0900

Composition of the ash:

SOLUBLE SALTS:	
Carbonic acid	19·498
Sulphuric acid	3·624
Phosphoric acid	none.
Potash	18·919
Soda	18·699
Chlorides of potassium and sodium	10·886
INSOLUBLE SALTS:	
Carbonate of lime	6·994
„ „ magnesia	1·814
Sulphate of lime	0·134
Phosphate of lime (tribasic)	17·634
„ „ magnesia	1·396
Perphosphate of iron	0·134
Silicic acid	0·268
	100·000

Calculated composition after deducting the carbonic acid:

Sulphuric acid	4·840
Phosphoric acid	11·916
Potash	24·739
Soda	24·451
Chlorides of potassium and sodium	14·235
Lime	17·608
Magnesia	1·728
Oxide of iron	0·077
Silicic acid	0·352
	100·000

XII.—CARROT (*Daucus carota*).

a.—1010·0 grs. of the fresh roots of the variety called the "Long Scarlet," gave 133·0 grs. of dry vegetable matter, and, upon incineration, 13·485 grs. of ash.

b.—12625·0 grs. gave 1662·0 grs. of dry matter, and 168·462 grs. of ash.

Mean per-centage of ash { from the fresh root 1·3340.
„ „ dried „ 10·1370.

Composition of the ash:

	I.	II.	MEAN.
SOLUBLE SALTS:			
Carbonic acid	16·261	16·263	16·262
Sulphuric acid	6·432	6·634	6·533
Phosphoric acid	4·309	4·099	4·204
Potash	13·001	14·005	13·503
Soda	23·909	23·437	23·673
Chloride of sodium.	7·321	7·301	7·311
INSOLUBLE SALTS:			
Carbonate of lime	7·420	7·430	7·425
„ „ magnesia	2·241	2·227	2·234
Sulphate of lime	traces.	traces.	traces.
Phosphate of lime (tribasic)	16·509	16·713	16·611
Phosphate of magnesia Perphosphate of iron	traces.	traces.	traces.
Silicic acid	2·205	2·195	2·200
	99·608	100·304	99·956

The following is the composition in 100 parts, after deducting the carbonic acid:

Sulphuric acid	8·239
Phosphoric acid	14·970
Potash	17·029
Soda	29·855
Chloride of sodium	9·220
Lime	16·523
Magnesia	1·341
Oxide of iron	traces.
Silicic acid	2·823
	100·000

XIII.—PARSNIP (*Pastinaca sativa*).

a.—1000·0 grs. of the fresh root gave 238·0 grs. of dry vegetable matter, and left, upon incineration, 14·12 grs. of ash.

b.—4965·2 grs. gave 1181·0 grs. of dry matter, and 70·10 grs. of ash.

Mean per-centage of ash { from the fresh roots 1·4130.
„ „ dried „ 5·9340.

The ash contained:

	I.	II.	MEAN.
SOLUBLE SALTS:			
Carbonic acid	14·062	14·264	14·163
Sulphuric acid	4 873	4·715	4·794
Phosphoric acid	5·706	5·352	5·529
Potash Soda	43·351	43·461	43·406
Chloride of sodium	3·806	3·756	3·781
INSOLUBLE SALTS:			
Carbonate of lime	7·760	7·820	7·790
„ „ magnesia	—	—	—
Sulphate of lime	traces.	traces.	traces.
Phosphate of lime (tribasic)	17·509	17·691	17·600
„ „ magnesia	traces.	traces.	traces.
Perphosphate of iron	2·915	2·899	2·907
Silicic acid	traces.	traces.	traces.
	99·982	99·958	99·970

Deducting the carbonic acid, the following composition in 100 parts is obtained:

Sulphuric acid	5·751
Phosphoric acid	18·270
Potash Soda	52·670
Chloride of sodium	4·588
Lime	16·811
Magnesia	traces.
Oxide of iron	1·910
Silicic acid	traces.
	100·000

XIV. POTATO (*Solanum tuberosum*).

I have analysed the ashes of the tubers of five different varieties of this plant, viz.: A. the "White Apple," B. the "Prince's Beauty," C. the "Axbridge Kidney," D. the "Maggie" or "Maghie," and E. the "Forty-fold." All of these were grown on the same soil, and under precisely similar circumstances.

A. *a.*—913·0 grs. of the fresh tubers of this variety, cut in thin slices, gave 247·0 grs. of dry vegetable matter, and left, upon incineration, 11·895 grs. of ash.

b.—7675·0 grs. gave 2074·7 grs. of dry matter, and 99·997 grs. of ash.

B. *a.*—693·0 grs. of the fresh tubers gave 202·5 grs. of dry vegetable matter, and 7·320 grs. of ash.

b.—1154·0 grs. gave 337·3 grs. of dry matter, and 12·298 grs. of ash.

C. *a.*—624·4 grs. of fresh tubers gave 182·3 grs. of dry vegetable matter, and 7·952 grs. of ash.

b.—1663·0 grs. gave 486·03 grs. of dry matter, and 21·163 grs. of ash.

D. *a.*—748·0 grs. of fresh tubers gave 236·3 grs. of dry vegetable matter, and 8·187 grs. of ash.

b.—3360 0 grs. gave 1062·93 grs. of dry matter, and 36·832 grs. of ash.

E. *a.*—596·0 grs. of fresh tubers gave 132·0 grs. of dry vegetable matter, and 5·25 grs. of ash.

b.—1430·4grs. gave 317·0 grs. of dry matter, and 12·6grs. of ash.

The following tables give a comparative view of the mean per-centage and composition of the ash from these five varieties of the potatoe :

Mean per-centage of ash :

	A.	B.	C.	D.	E.
From the fresh tubers .	1·3029	1·0609	1·2709	1·0953	0·8808
„ „ dried „	4·8180	3·6304	4·3581	3·4648	3·9750
Composition of the ash :					
SOLUBLE SALTS :					
Carbonic acid . .	21·059	16·666	21·400	18·162	13·333
Sulphuric acid . .	2·774	4·945	3·244	5·997	6·780
Phosphoric acid . .	5·716	8·920	3·774	6·669	11·428
Potash . . .	53·467	54·166	55·610	55·734	53·029
Soda	traces.	traces.	traces.	traces.	traces.
Chloride of sodium .	traces.	traces.	traces.	traces.	2.095
INSOLUBLE SALTS :					
Carbonate of lime .	0·844	2·019	3·018	1·954	2·286
„ „ magnesia.	3·530	0·273	1·257	2·565	0·570
Sulphate of lime . .	traces.	traces.	0·125	traces.	traces.
Phosphate of lime (tribasic)	3·363	0·683	3·835	5·374	2·856
Phosphate of magnesia.	9·247	12·298	7·550	3·545	7·623
Perphosphate of iron .	traces.	traces.	0·062	traces.	traces.
Phosphate of alumina .	traces.	—	—	—	traces.
„ „ manganese	—	—	—	—	traces.
Silicic acid. . .	traces.	traces.	0.125	traces.	traces.
	100·000	100·000	100·000	100·000	100·000

	A.	B.	C.	D.	E.
Sulphuric acid . .	3·615	6·007	4·329	7·530	7·942
Phosphoric acid . .	17·222	20·831	14·892	14·363	20·677
Potash . . .	69·688	65·823	70·590	69·985	62·118
Soda . . .	traces.	traces.	traces.	traces.	traces.
Chloride of sodium .	traces.	traces.	traces.	traces.	2·454
Lime . . .	2·976	1·843	4·969	5·009	3·301
Magnesia . . .	6·499	5·496	5·014	3·113	3·508
Oxide of iron . .	traces.	traces.	0·043	traces.	traces.
Alumina . . .	traces.	—	—	—	traces.
Oxide of manganese .	—	—	—	—	traces.
Silicic acid . . .	traces.	traces.	0·163	traces.	traces.
	100·000	100·000	100·000	100·000	100·000

If we consider attentively the results contained in the preceding pages, we shall arrive at the following general conclusions:

1. That the inorganic constituents differ both in proportion and composition in each of the crops examined.

2. That cultivation can, to a very considerable extent, modify and control the assimilative powers of plants for certain inorganic substances.

This is most decisively proved in the case of the potato plant (No. XIV), in which neither the proportion nor chemical composition of the ashes from any two varieties are alike. True it is, that there is, in many respects, a great resemblance to be detected in all of them, but the differences are still much too great to be overlooked.

It would be extremely interesting to ascertain, by direct experiment, whether the various varieties of plants which occur naturally, (and which, therefore, cannot be the result of cultivation), likewise contain different inorganic constituents, as if such were proved to be the case, it would, in my idea, go far to explain to us the cause of the formation of varieties in the vegetable kingdom, which is, at present, except in a few instances, an almost inscrutable mystery.

This influence of cultivation on plants is of great practical importance in agriculture, for as the evident object of the farmer's endeavours, is to obtain the greatest amount of produce from his land at the least possible expenditure of time and money, so does it become necessary for him, in order to effect this, to ascertain the variety of the plant which is best suited to his soil; for, by substituting one variety for another, he may often obtain as large a crop, at as early a season, and, at the same time, be enabled to effect a great economy in the application of his manures. Hence also he must not take it for granted, because one variety of a plant does not happen to succeed, that, therefore, his land is not adapted for the cultivation of that particular vegetable; for where one variety will utterly fail, another will often yield an admirable crop.

Another remarkably good instance of the change produced by cultivation in the inorganic constituents of plants is exhibited in the two asparagus plants (No. IV), where it will be observed, that the soda and lime-salts of the wild specimen (II) have been to a very considerable extent replaced by potash-salts in the cultivated plant (I). These results would not, however, appear to be in accordance with the law, or rather hypothesis, recently advanced by Professor Liebig; namely, that the sum of the oxygen in the bases in combination with the organic acids (which occur as carbonates in the ash) is constant in the same species of plant, no matter what the nature of the soil may be upon which the individual specimens are grown; for it will be seen, that whilst the ashes of the cultivated plant contained

14·269 grs. of CO^2 in the soluble salts = 5·1887 grs. of O in base.
14·611 grs. of CO^2+CaO = 2·3370 „ „

Sum of oxygen 7·5257

those of the wild specimen, on the contrary, contained only
4·861 grs. of CO^2 in the soluble salts = 1·7670 grs. of O in base.
21·432 grs. of CO^2+CaO = 3·4290 „ „
2·617 grs. of CO^2+MgO = 0·4940 „ „

5·6940

or nearly two per cent less in the total proportional of oxygen—a difference evidently much greater than can be attributed to the errors of analysis only.

I intend, however, if my time will allow me, to make a much more extensive series of experiments on this subject in the course of another year, when I hope to communicate the results to the Society.

3. That the principal, and by far the most important, constituents of root crops, are the alkalies, potash and soda, which occur for the greater part free, the remainder being in combination with sulphuric and phosphoric acids. They generally form from 43 to 71 per cent of the ash.

It must not be imagined, however, that all the alkali, which was estimated in the ash as carbonated, existed in the living plant in combination with organic acids, part of it was evidently produced by the decomposition of the nitrates by the carbon of the vegetable matter. In such large quantities, in fact, did the nitrates occur in the case of the radish (No. XI), that actual scintillations were observed to take place upon incinerating the dried plant. By a proximate analysis, I found the dried roots to contain from 13 to 14 per cent of the mixed nitrates of potash and soda.

4. That in the potato (No. XIV), the lime, except in one instance, is greatly exceeded in quantity by the magnesia; sometimes even in the proportion of three to one.

If we examine, we shall see that this observation is likewise borne out by the experiments of other chemists. Thus, Boussingault found the relation of the former to the latter earth to be as 1·8 to 5·4; and Daubeny, in three analyses, found respectively 2·71, 3·67, and 2·54 per cent of lime, and 10·98, 7·00, and 6·31 per cent of magnesia.

In fact, magnesia would appear to be necessary for the growth and well-being of the potato-plant, as it has been observed, that when it is not present in the soil in sufficient quantity, the tubers rarely if ever attain their full development.

5. That the alkaline chlorides are present in greater or smaller quantity in all the crops examined.

Although these sometimes occur to such an extent as to form more than half the entire weight of the ash, I think it is a great question whether they perform any important part in the organism of the plant. Indeed, judging from the manner in which they are observed to fluctuate in quantity in different specimens of the same plant, I am inclined to believe, that in the majority of cases, (if we except those plants of marine origin, such as the sea-kale, asparagus, &c., to which they are essential), they ought to be classed amongst those substances, which, from their extreme solubility, are absorbed by the roots of plants, and are thus carried into the system, without being actually necessary either for their health or existence. In proof of this opinion, Daubeny found in three analyses of the ashes of turnip-roots, 5·4 per cent of chloride of sodium in one, and none in either of the others; and in the three specimens of potato-ashes before mentioned, that gentleman found respectively 8·75, 5·88, and 1·87 per cent of mixed chlorides: I found in five analyses 2·454 in one, and only traces in the other four. In the ashes of the roots of the carrot and parsnip, Sprengel found 1·76 and 7·15 per cent of chloride of sodium; I found 9·22 and 4·588 per cent.

6. That in all young succulent shoots, as in root crops, the alkalies and alkaline salts greatly exceed in quantity the insoluble earthy and metallic salts.

I have already attempted to explain the reason of this in a former paper.

The sulphuric and phosphoric acids are also present in rather considerable proportion, especially in the sea-kale and asparagus (Nos. III and IV), where they amount to from 40 to 43 per cent of the ash. The great relative increase of these acids and potash observed in the young, as compared with the old, plant of sea-kale, was no doubt occasioned by the salts of the animal manure with which the former had been supplied.

In order to render these analyses of practical utility to the farmer and horticulturist, I have annexed a table showing the relative quantities of manure requisite for a ton weight of each of the vegetables examined in the fresh state; from which it will, of course, be easy for him to calculate, by means of a simple rule-of-three sum, the weight necessary to be applied to his land per acre for any particular crop.

I need hardly say that these calculations do not pretend to any extraordinary accuracy; they must only be considered as approximations to the truth.

TABLE SHOWING THE PROPORTION AND COMPOSITION OF THE MANURES REQUIRED FOR A TON WEIGHT OF THE FRESH VEGETABLE, GIVEN IN AVOIRDUPOIS POUNDS AND OUNCES.

	Sea-kale.	Celery.	Asparagus.	Cauliflower, entire plant.	Kidney bean, legumes.	Onion.	Garden turnip.	Swede turnip.
	Young sprouts.					Roots.		
Pearl-ash	1·9½	10·8½	11·2¼	5·6	7·6¾	6·4	8·4¾	20·4½
Soda-ash	1·10	—		—	—	—	—	—
Glauber's salts (SO³, NaO + 10 HO)	14.3½	0·13		8·14½	—	—	—	—
Epsom salts (SO³, MgO + 7 HO)	—	—		—	1·11	2·7	1·12	3·7½
Common salt	—	7·15¾	1·13½	1·4	0·11¼	0·5½	1·11¾	1·10½
Lime	—	—	—	—	1·8¼	0·1¼	—	—
Gypsum (SO³, CaO + 2 HO)	—	—	—	—	—	—	—	—
Bone-earth	6·9	6·12½	3·13½	7·8¾	2·2⅓	4·4¼	4·3¾	7·3
Carbonate of magnesia	—	—	—	—	—	—	—	—
Oxide of iron	—	—	0·0½	0·2	—	—	—	0·1
Silica	0·11	0·6¼	0·2¾	0·4	0.4½	0·0¼	0·2½	0·0½
	24·11	26·7¾	17·0½	23·7¼	13·12¼	13·6¼	16·2¾	32·11
Actual quantity of real inorganic constituents in same weight of fresh vegetable	15·2	21·12¾	16·15	15·11¾	10·8	9·15¾	11·14¼	22·0½

	Beet.	Radish.	Carrot.	Parsnip.	Potato, Tubers, Varieties.				
	Roots.				White apple.	Prince's Beauty.	Axbridge kidney.	Maggie or Maghie.	Forty-fold.
Pearl-ash	12·15	5·1½	5·14	about 18·7	22·9¾	18·11	22·8¼	19·14	15·3½
Soda-ash		5·9½	10·3		—	—	—	—	—
Glauber's salts	—	0·12	5·5¾	6·1	—	—	—	—	—
Epsom salts	2·12	1·8¼	1·14¾	—	5·4	3·10¼	2·14	4·6	4·1½
Common salt	1·5	2·0¼	2·3	1·3	—	—	—	—	0·6½
Lime	—	—	—	—	—	—	—	—	—
Gypsum	6·0	—	—	—	—	—	—	—	—
Bone-earth	2·7	5·0¼	7 12½	10·4½	8·2½	8·13	7·0½	6·1½	7·9¾
Carbonate of magnesia	—	—	—	—	2·1½	1·1	1·6	—	—
Oxide of iron	—	—	—	0·8	—	—	0·0¼	—	—
Silica	—	0·0¼	0·10½	—	—	—	0·0¾	—	—
	25·7	20·0½	33·15½	36·7½	38·1½	32·3¼	33·13¾	30·5½	27·4¾
Actual quantity of real inorganic constituents in same weight of fresh vegetable	16·2¼	14·2½	23·11½	26·0¾	22·4	19·7½	21·13¾	19·8¼	16·13½

Dec. 4, 1848.

The President in the Chair.

Mr. Brodie presented a copy of his paper, "Investigations of the chemical properties of Wax," to the Library; Mr. W. Sykes Ward presented his Balance Galvanometer to the Museum. Messrs. E. Pontifex and Ralph Busby were elected members of the Society.

The following papers were read:

On a Balance Galvanometer. BY WILLIAM SYKES WARD, ESQ.—No recognised method being known by which the working effects of various voltaic arrangements can be referred to a common standard, it occurred to the author of this paper, that this might be more easily effected by means of a new form of galvanometer than by any other.

The new galvanometer proposed, consists of a coil of covered copper wire, in the form of a long parallelogram, the ends of the wire being extended so as to form pivots on which the coil swings, and which pivots also form the connections for the current to pass through the coil and its supports. To the coil are appended two short arms, forming a kind of balance-beam to which small scale-pans are attached. The two poles of a horse-shoe magnet of moderate power are inserted within the coil, so as to allow it a moderate range of vibration, and the force of the current is measured by the weight in grains supported in the scale-pans.

The galvanometer is recommended on account of the facility with which coils, containing various lengths of wire and of different thickness or resistance can be adapted and readily changed, as most suited for any experiment, and it is frequently found advisable to use a coil having about the same resistance as the other resistances of the circuit; although for general purposes it is most advisable to have two coils, one consisting of 10 feet of copper wire of No. 20 Birmingham wire guage, of which 1 foot weighs 27·4 grains, for estimating quantity, and another of 100 feet of about No. 35, or $\frac{1}{120}$th of an inch, of which one foot weighs 97 grains, for estimating intensity or electro motive force; the former wire may be covered with cotton; the latter should be well, but lightly covered with silk. The magnet should be so strong, that the indications may be manifested by considerable weights; but it should not be too highly or nearly saturated, or charged with magnetism, as its power would then be very liable to be impaired by use or by time.

Several coils or bundles of wire similar to that of the moveable coils, and of precisely the like resistance, should also be provided.

The coils are made most advantageously by winding the wire upon a parallelogram of wood, about three inches long, and half an inch thick, and of about twice the width of the coil, slightly tapering towards one side, to facilitate the removal of the coil. A layer of the insulated wire is wound upon the parallelogram, and slightly cemented with shell-lac; another layer of wire is then wound upon the first, which is again cemented, and so on, until sufficient wire has been added. The coil being carefully removed from the block on which it has been formed, two bent needles are attached to the sides, to form pivots, having the points of the needles a little above the centre of gravity of the coil, which needles are adjusted by bending, so that the coil may hang horizontally. The needles or pivots for the coils of thin wire answer best when made of platinum. Around the pivots a portion of the uncovered end of the wire is wrapped, so as to dip into mercury, placed in small conical holes, in which the ends of the needles are supported.

If magnets could, with certainty, be obtained of precisely the same power, a standard pattern might be agreed upon for the coils, and uniform instruments procured. The value of the indications can, however, readily be modified in weight, by altering the length of the arms to which the scale-pans are attached; and it is proposed that the galvanometer be adjusted to a common standard, by making a grain weight, supported by the 10-feet coil, the equivalent to 1 grain of zinc, consumed in a single voltaic combination in one hour.

The galvanometer may, therefore, be adjusted by employing a pair of elements, the zinc of which has been weighed; the circuit is then completed with a galvanometer, and allowing the action to continue for one hour, or any convenient part of an hour, from time to time the weights counterpoised by the current are observed and noted down, an average being obtained by interpolation; the zinc being taken out and weighed, the ratio between the number of grains dissolved and the weight in the scale-pan will be ascertained. If this be a convenient number for reduction, the galvanometer will be retained in its then state, and the observations reduced, or the arms of the balance, which I have found may be fixed sufficiently by shell-lac, are altered in length until the indications correspond—grain balanced for grain dissolved.

This may be perhaps more easily understood by a practical example. A small arrangement of the nitric acid battery was used, in which a sheet of platinum surrounded the porous cell, and a narrow strip of zinc was placed within the cell. In the first instance the zinc weighed 114 grains.

	h	m			
At	8	27	the galvanometer balanced	57	grains
„	8	35	„	54	„
„	8	40	„	58	„
„	8	50	„	57	„
„	8	57	„	57	„
				5) 283	„
				56·6	

The zinc then weighed 83 grains, 31 having been dissolved: thus the instrument, instead of having balanced 62 grains on the average, had only balanced 56·6, and therefore required adjusting, either by altering the position of the magnet, or altering the length of the arms of the balance, which, for this purpose, consisted of two thin slips of brass, each cemented with shell-lac on a thin piece of wood, the piece of wood being cemented to the coil: thus the small brass arm being warmed in the flame of a lamp, the length of the arm, from the pivot, is easily altered without affecting the wrapping of the coil.

It was also proved by experiment that, within very considerable limits, the weight balanced by the galvanometer may be relied on as indicating the quantity of current passing.

The relative indications of the galvanometer and the voltameter were likewise compared, and the author arrived at the conclusion, that this form of galvanometer will give much more accurate indications than can be obtained from a voltameter, in addition to the advantage it presents of affording results more immediately, and interposing less additional resistance in the circuit.

II.—*On the action of Baryta on Salicylic Ether.* By G. Baly, Esq.

One of the most interesting facts with which we have become acquainted by the investigations of M. Cahours,* is the remarkable decomposition which the oil of *Gaultheria procumbens* (salicylate of oxide of methyl) undergoes when subjected to the action of alkaline earths at a high temperature. On performing this experiment, M. Cahours obtained a fluid possessing all the properties of anisol, a substance which he had previously discovered in acting with baryta upon anisic acid.

Gaultheria oil and anisic acid are isomeric, the composition of both these substances is expressed by the formula

$$C_{16}\,H_8\,O_6,$$

but nobody can mistake the difference in their molecular arrangement, and it was certainly a startling result to see two such dissimilar compounds exhibiting the same behaviour when under the influence of powerful agents.

The identity in the products of decomposition of these isomeric bodies is by no means an isolated fact; several cases of a similar nature have since been observed. Anthranilic acid and nitrotoluol, are likewise isomeric, and no two bodies could present a more striking dissimilarity in constitution; nevertheless both these compounds, when subjected to the action of heat, undergo, as pointed out by Drs. Hofmann and Muspratt,* exactly the same decomposition, they are split into aniline and carbonic acid.

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* Ann. de Chimie et Phys. 3ème Sér. t. x. p. 327.

In his memoir on gaultheria oil, M. Cahours mentions that salicylate of oxide of ethyl, when acted on by baryta, undergoes a similar decomposition to the methyl compound; an oily liquid, insoluble in alkalies, is produced, carbonate of baryta remaining in the retort. It appeared extremely probable that the compound thus obtained was an analogue of phenol and anisol, containing two more equivalents of carbon and hydrogen than the latter substance. M. Cahours not having prosecuted this investigation, Dr. Hofmann invited me to prepare the compound, in order to establish its composition by an analysis, and study its properties.

The salicylic acid used for the following experiments, was prepared from gaultheria oil, which readily yields this acid in a state of perfect purity. Salicylic acid is etherified with great facility. By distilling a mixture of salicylic acid, alcohol and sulphuric acid, I obtained the ether with all the properties M. Cahours mentions. The boiling point of the pure liquid was constant at 229°·5 C = (444° F.), a few degrees higher than the temperature specified by M. Cahours, who found it to be 225° (437° F.). The specific gravity of the ether is 1·097.

On mixing pure salicylic ether with anhydrous baryta, a very considerable evolution of heat takes place, sufficient to effect complete decomposition, unless the experiment be made with small quantities at a time. In order to avoid loss, it is necessary to add the ether drop by drop to the baryta, until an increase of temperature is no longer observed on further addition. In this manner a dry solid compound of the ether with baryta is obtained, corresponding evidently to the gaultherate of baryta, obtained by acting in the same manner on the methyl compound. On distilling this compound in a small glass retort, a brownish yellow liquid passes over, possessing a strong odour of phenol. The distillate thus obtained is a mixture of two liquids, of which the one is soluble in potash, and presents all the properties of phenol, whilst the other is a liquid of an agreeable odour, for which I propose the name of *salithol,* in order to indicate that it is formed from salicylic ether.

Salithol is easily purified; for this purpose the crude product of the distillation is treated with a dilute solution of potash, which removes at once the odour of phenol, that substance being dissolved, leaving a yellow layer of oil on the top of the liquid. The oil is washed with water, separated by means of a pipette, dried over fused chloride of calcium, and finally rectified.

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* Memoirs of the Chemical Society of London, v. ii. p. 249.

Salithol, when pure, is a colourless liquid of a very agreeable aromatic odour. Its boiling point is 175° C. (347° F.) An analysis, by combustion with oxide of copper, gave the following results.

I. 0·1915 grm. of substance gave
0·5515 „ carbonic acid, and
1·1450 „ water.
II. 0·1938 „ of substance gave
0·5575 „ carbonic acid, and
0·1490 „ water.

Per-centage composition:

	I.	II.
Carbon . . .	78·54	78·45
Hydrogen . . .	8·41	8·54

These numbers closely correspond with the formula

$$C_{16}\,H_{10}\,O_{2},$$

as may be seen from the following table:

	Theory.		Mean of experiments.
16 eq. of carbon . . .	96 =	78·68	78·49
10 „ of hydrogen . .	10 =	8·19	8·47
2 „ of oxygen . .	16 =	13·13	13·03
1 „ of Salithol . .	122	100·00	99·99

The formation of salithol is perfectly analogous to the production of phenol from salicylic acid, and of anisol from anisic acid, or salicylate of oxide of ethyl. This will be evident from the following formulæ:

$$\underbrace{C_{14}\;H_{6}\;C_{6}}_{\text{Salicylic acid.}} + 2\;BaO = 2\;BaO\,CO_{2} + \underbrace{C_{12}\;H_{6}\;R_{2}}_{\text{Phenol.}}$$

$$\underbrace{C_{16}\;H_{8}\;O_{6}}_{\text{Anisic acid.}} + 2\;BaO = 2\;BaO\,CO_{2} + \underbrace{O_{14}\;H_{8}\;O_{2}}_{\text{Anisol.}}$$

$$\underbrace{C_{18}\;H_{10}\;O_{6}}_{\text{Salicylic ether.}} + 2\;BaO = 2\;BaO\,CO_{2} + \underbrace{C_{16}\;H_{10}\;O_{2}}_{\text{Salithol.}}$$

The simultaneous production of phenol arises from part of the salicylic ether being converted into salicylate of baryta, when acted on by caustic baryta.

It is very probable that the progress of science will make us acquainted with an acid isomeric with salicylate of ethyl, and belonging to the series of acids with six equivalents of oxygen, of which salicylic and anisic acids are as yet the only members. An acid of this composition when distilled with baryta would evidently likewise be converted into salithol.

I should have liked to control the formula of salithol by the study of some of its products of decomposition, the difficulty however of obtaining it in sufficient quantity, has prevented me from entering more minutely into the investigation.

Chlorine acts very powerfully on salithol; heat is evolved during the reaction, and hydrochloric acid disengaged, a viscid mass being produced, which after standing for several weeks, shewed a tendency to crystallize.

Bromine forms, in the same manner, a heavy oily compound with salithol, which solidifies after a few days to a hard crystalline mass, soluble in boiling alcohol, from which it crystallizes on cooling. The appearance of the crystals thus deposited, as well as the results of several combustions, indicated that the action of bromine gave rise to the formation of various compounds. It is very likely that a series of substitution-products like the following

$$C_{16}\left\{\begin{matrix}H_9\\Br\end{matrix}\right\}O_2.$$

$$C_{16}\left\{\begin{matrix}H_8\\Br_2\end{matrix}\right\}O_2$$

$$C_{16}\left\{\begin{matrix}H_7\\Br_3\end{matrix}\right\}O_2$$

may be formed in this manner. The small quantity of material at my disposal did not admit of their separation by repeated crystallization.

DINITRO-SALITHOL.

Fuming nitric acid dissolves salithol, producing a liquid of a beautiful violet colour, which colour disappears completely on the application of heat. By ebullition, the whole of the salithol is converted into a crystalline mass, which is insoluble in water, but dissolves in boiling alcohol, from which it is deposited, on cooling, in needle-shaped crystals. These crystals likewise consist of various compounds; if however the ebullition with nitric acid has been continued for some time, a product is obtained which, after being washed with water, and crystallized two or three times from alcohol, seems to be nearly pure dinitro-salithol.

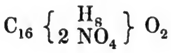
By burning two products, obtained at different times with oxide of copper, in the above manner, the following results were obtained:

I. 0·200 grm. substance gave
0·316 „ carbonic acid, and
0·074 „ water.
II. 0·282 „ substance gave
0·452 „ carbonic acid, and
0·1015 „ water.

Per-centage composition:

	I.	II.
Carbon	43·09	43·71
Hydrogen	4·11	3·99

The formula



$$C_{16}\left\{\begin{matrix}H_8\\ 2\,NO_4\end{matrix}\right\}O_2$$

requires

Carbon	45·28
Hydrogen	3·77

The deficiency in the carbon probably arises from an admixture of trinitro-salithol. Unfortunately, the last portion of my substance being consumed, I was prevented from repeating the analysis with a purer product.

III.—*Analysis of the Water supplied by the Hampstead Water-works Company. By* John Mitchel, Esq.

The deep well water from Messrs. Combe and Delafield's Brewery, has been analysed by Professor Graham, and the water of the Artesian Wells at Trafalgar Square by Messrs. Abel and Rowney, as well as that of the Thames by Mr. Clark, but I am not aware that the waters supplied by the London Water Companies have yet been subjected to analysis. It was thought that such a series of analyses would be an useful addition to those already cited, not only in a scientific, but also in a sanatory point of view. The present communication, the first of the series, has reference to an examination of the water supplied by the Hampstead Water-works Company. The water was not taken direct from the works, but analyzed as supplied to the house; the chief object being to ascertain whether the water in question possessed any power of taking up lead or zinc, as I had been informed on the authority of a plumber in the neighbourhood, that such was the case with reference to the former metal, I have found that, as far as the water analyzed was concerned, no perceptible action was exerted, and I am the more induced to believe this correct, from the circumstance that several leaden cisterns have been for a great number of years continually subjected to its influence, and do not appear affected in the slightest degree. This may be in some measure explained by the comparatively large quantity of soluble sulphates contained in the water, as it has been shewn by Dr. Christison, that water containing even a small amount of sulphates is comparatively without action on metallic lead.

The water is pumped continuously from a plain bore-hole at the Works in Pond Street, Hampstead, and is obtained partly from the sand and partly from the chalk.

The specific gravity of the water at 58° F. is 1000·65, distilled water being 1000.

Qualitative analysis exhibited the presence of magnesia, lime, potash and soda, with sulphuric, silicic and carbonic acids, chlorine organic matter, and a trace of phosphoric acid.

A. Determination of the total amount of fixed constituents.

Amount of water.	Fixed residue.	Per-centage.
I. 4000 grs.	2·284 grs.	0·0571
II. 3500 ,,	2·002 ,,	0·0575
		Mean 0·0573

B. Determination of sulphuric acid.

Amount of water.	Sulphate of baryta.	Per-centage of Sulphuric acid.
I. 4000 grs.	1·136 grs.	0·0097524
II. 3981 ,,	133·1 ,,	0·0097504
		Mean 0·0097514

C. Determination of chlorine.

Amount of water.	Amount of chloride of silver.	Chlorine per cent.
I. 3524 grs.	2·216 grs.	0·01555
II. 4120 ,,	2·590 ,,	0·01567
		Mean 0·01566

D. Determination of the silicic acid.

Amount of water.	Amount of silicic acid.	Silicic acid per cent.
I. 8750 grs.	0·032 grs.	0·00040685
II. 10000 ,,	0·041 ,,	0·00041000
		Mean 0·00040842

E. a. Determination of the total amount of lime.

	Amonnt of water.	Amount of carbonate of lime.	Lime per cent.
I.	7850 grs.	0·801 grs.	0·005717
II.	10000 „	1·020	0·005615
		Mean	0·005666

A given quantity of water was boiled for half an hour, the flask being so arranged that no evaporation could take place. The precipitate formed was separated by filtration, and the amount of lime in the precipitate and filtrate determined in the usual manner.

b. Estimation of lime in the precipitate.

Amount of water.	Amount of carbonate of lime.	Per-centage of lime in the water as carbonate.
8000 grs.	0·438 grs.	0·003056

c. Determination of lime in filtrate.

Amount of water.	Amount of carbonate of lime.	Per-centage of lime in the water as soluble salts.
8000 grs.	0·371 grs.	0·0025997

F. Determination of magnesia.

Amount of water.	Pyro-phosphate of magnesia.	Per-centage of magnesia.
7850 grs.	0·505 grs.	0·002355
10000 „	0·644 „	0·002357
	Mean	0·002356

G. Determination of the alkalies.

Amount of water.	Amount of chlorides of potassium and sodium.
10000 grs.	3·475 grs.
8000 „	2·782 „

a. Estimation of potash.

Amount of water.	Potassio-chloride of platinum.	Per-centage of potash.
10000 grs.	1·313 grs.	0·0025335
8000 „	1·050 „	0·0025326
	Mean	0·0025330

b. Estimation of soda.

Amount of water.	Chloride of sodium.	Per-centage of soda.
10000 grs.	3·074 grs.	0·0016193
8000 „	2·450 „	0·0016232
	Mean	0·00162125

H. Determination of carbonic acid.

This was determined in the usual manner, by the addition of a mixture of chloride of calcium and ammonia to a known weight of water. 21000 grs. of water, thus treated, gave 8·21 grs. of precipitate, which, by the ordinary process, yielded 1·456 grs. of carbonic acid, = 0·006938 per cent. of that body in the water.

In order to determine the phosphoric, crenic and apocrenic acids, and extractive matter, 100 lbs. of the water were evaporated to 2 lbs., giving 72 grs. of precipitate, the filtrate and washings weighing 25000 grs.

I. Determination of phosphoric acid in combination with lime.

Amount of precipitate.	Pyro-phosphate of magnesia.	Per-centage of phosphoric acid.
17 grs.	1·016 grs.	0·000392

K. Determination of organic matter.

a. Apocrenic acid.

Amount of precipitate.	Copper-salt obtained.	Per-centage of apocrenic acid.
22·2 grs.	0·320 grs.	0·00012005

b. Crenic acid.

Amount of precipitate.	Copper-salt obtained.	Per-centage of crenic acid.
22·2 grs.	1·986 grs.	0·000237

c. Extractive matter.

Amount of filtrate.	Extractive matter.	Per-centage of extractive matter.
10000 grs.	6·88 grs.	0·0002457.

According to the above results, the water contains per imperial gallon in grains:

Carbonate of lime . . .	3·83250
Carbonate of magnesia . .	3·40830
Phosphate of lime . . .	·27672
Sulphate of lime . . .	4·42018
Sulphate of potash . . .	3·27812
Sulphate of soda . . .	4·81130
Chloride of sodium . . .	17·75814
Silica acid	·28589
Crenic acid	·16590
Apocrenic acid . . .	·08403
Extractive matter . . .	1·71990
Oxides of iron and manganese. .	traces
	40·04110

The amount of fixed residue obtained by direct experiment was 40·11 grs. per gallon.

The amount of pure carbonic acid in the water is 4·39 cubic inches in the imperial gallon.

Dec. 18, 1848.

John Thomas Cooper, Vice-President, in the Chair.

Messrs. John Blyth, M.D., F. Muspratt, J. H. Gladstone, Ph. D., James Napier, James Mason, and William Reylin, were elected Members of the Society.

The following paper was read:

IV.—*Researches on the volatile Organic Bases.*]

By Dr. A. W. Hofmann;

Professor at the Royal College of Chemistry.

IV. ANILIDES.

In a short note,* communicated several years ago to the Society, I pointed out the existence of several new aniline compounds, without entering, however, into details respecting their properties, and without giving the analytical data on which my statements were founded.

A variety of other researches prevented me from completing the study of these substances, and it was but of late, that a new reaction I met with in another investigation, compelled me to return to the subject.

In my paper on melaniline,† I mentioned that the result of the action of chloride of cyanogen on aniline is very materially influenced by the presence of even small quantities of water, either in the aniline or in the chloride of cyanogen. Perfectly anhydrous aniline, when exposed to the action of chloride of cyanogen, previously dried by chloride of calcium, is entirely converted into hydrochlorate of melaniline, in accordance with the formulæ:

$$2\,\underbrace{(C_{12}\,H_7\,N)}_{\text{Aniline.}} + \underbrace{C_2\;N\;Cl}_{\text{Chloride of Cyanogen.}} = \underbrace{C_{26}\,H_{13}\,N_3,\;H\,Cl,}_{\text{Hydrochlorate of Melaniline.}}$$

On separating the base, by means of potash, from the solution of this hydrochlorate, a mother-liquor is obtained, which, on evaporation, yields scarcely a trace of organic matter.

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* Memoirs of the Chemical Society, vol. III. p. 26.

† Quarterly Journal of the Chemical Society, vol. I. p. 286.

Action of chloride of cyanogen on aniline in the presence of water.—If the action of chloride of cyanogen on aniline takes place in the presence of water, a different deportment is observed. The mother-liquor, from which the melaniline has been separated by an alkali, when concentrated by evaporation, deposits on cooling slightly coloured acicular crystals, the quantity of which is in direct proportion with the amount of water that has been present. By treating aniline with the aqueous solution of chloride of cyanogen, obtained by passing chlorine gas into a solution of hydrocyanic acid in water, the chief product of the reaction, besides hydrochlorate of aniline, consists in the above-mentioned acicular crystals, whilst only traces of melaniline are separated on the addition of potash. The acicular crystals, as will be seen from the subjoined analysis, are the anomalous cyanate of aniline or anilo-urea, as the compound formerly was briefly termed.

ANILO-UREA.—CARBAMIDE-CARBANILIDE.

There is no difficulty in purifying the crystals of this substance. Treatment with animal charcoal, and one or two crystallizations, from boiling water, are sufficient to render them perfectly colourless.

The same compound is produced by mixing a solution of sulphate of aniline and cyanate of potash. After the lapse of some time the liquid becomes turbid, and gradually solidifies into a crystalline mass, consisting of the new substance and sulphate of potash, which have separated by crystallization, the former being very soluble in boiling, and but slightly soluble in cold water.

A third method of preparing it, consists in passing the vapour of hydrated cyanic acid (as obtained in the distillation of cyanuric acid) into anhydrous aniline. This experiment, however, requires particular care; the liquid has to be kept as cool as possible. On passing a rapid current of cyanic acid gas into the base, a very powerful evolution of heat takes place, under the influence of which, the newly-formed compound undergoes a further decomposition, a substance perfectly insoluble in water being formed, to which I shall return in the course of this paper. If the liquid has been exposed to a slow stream of gas, it gradually solidifies into a crystalline mass, which, when dissolved in boiling water, deposits crystals of perfect purity on cooling. In most cases, however, a small quantity of the substance insoluble in water is likewise formed.

The identity of these products was proved by the following analyses.

For the analyses I. II. and IV., the compound had been prepared by the action of moist chloride of cyanogen on aniline; analysis III. refers to a product obtained by treating aniline with a current of cyanic acid gas.

I. 0·3667 grm. of substance gave:
0·8247 „ „ carbonic acid, and
0·1995 „ „ water.
II. 0·2905 „ „ substance gave:
0·6590 „ „ carbonic acid, and
0·1610 „ „ water.
III. 0·2878 „ „ substance gave:
0·6456 „ „ carbonic acid, and
0·1595 „ „ water.
IV. 0·2947 „ „ substance gave:
0·4262 „ „ platinum.

From these numbers the following per-centage composition is deduced:

	I.	II.	III.	IV.
Carbon . .	61·33	61·86	61·17	—
Hydrogen . .	6·04	6·15	6·15	—
Nitrogen . .	—	—	—	20·51

which leads to the formula:

$$C_{14}\, H_8\, N_2\, O_2,$$

as may be seen from the following table:

	Theory.		Mean of experiments.
14 equiv. of Carbon . .	84	61·76	61·45
8 „ „ Hydrogen .	8	5·88	6·08
2 „ „ Nitrogen . .	28	20·58	20·51
2 „ „ Oxygen . .	16	11·78	—
1 „ „ Anilo-urea .	136	100·00	

The formation of anilo-urea in the preceding reactions is easily intelligible; whilst in the two latter cases it is produced either by the direct union of the constituents:

$$\underbrace{C_{12}\, H_7\, N}_{\text{Aniline.}} + \underbrace{H\, C_2\, N\, O_2}_{\text{Cyanic acid.}} = \underbrace{C_{14}\, H_8\, N_2\, O_2}_{\text{Anilo-urea.}},$$

or by a process of double decomposition:

$$\underbrace{C_{12}\, H_7\, N, H\, S\, O_4}_{\text{Sulphate of aniline.}} + \underbrace{K\, C_2\, N\, O_2}_{\text{Cyanate of potassa.}} = \underbrace{C_{14}\, H_8\, N_2\, O_2}_{\text{Anilo-urea.}} + K\, S\, O_4,$$

we have in the former, a transposition of the chloride of cyanogen with the elements of water, in consequence of which hydrochloric acid and cyanic acid are formed:

$$2\,\underbrace{C_{12}H_7N}_{\text{Aniline.}} + \underbrace{C_2NCl}_{\substack{\text{Chloride of}\\ \text{Cyanogen.}}} + 2\,HO = \underbrace{C_{12}H_7N, HCl}_{\substack{\text{Hydrochlorate of}\\ \text{Aniline.}}} + \underbrace{C_{14}H_8N_2O_2}_{\text{Anilo-urea.}}$$

The exchange of chlorine for oxygen in this case is remarkable; it does not occur in the presence of ammonia; by saturating an aqueous solution of ammonia with chloride of cyanogen and subsequent evaporation I did not obtain crystals of urea.

Anilo-urea is but sparingly soluble in cold water; boiling water dissolves it in large quantities; if the saturated solution be boiled with an excess of the substance, the crystals fuse and sink to the bottom of the vessel in the form of an oily fluid. The compound is likewise very soluble in alcohol and ether. It can be boiled with dilute acids and alkalies, without the slightest decomposition. I have repeatedly studied this reaction, because at the first glance it appeared to point out the possibility of thus producing anthranilic acid:

$$\underbrace{C_{14}H_8N_2O_2}_{\text{Anilo-urea.}} + 2\,HO = \underbrace{C_{14}H_7NO_4}_{\substack{\text{Anthranilic}\\ \text{acid.}}} + NH_3\,?$$

I have not, however, been able to effect this transposition; both alkalies and acids, when employed in concentrated solutions, produce different changes.

When boiled with a concentrated solution of potash, or when heated with hydrate of potash, anilo-urea yields aniline and ammonia, carbonate of potash remaining in the retort:

$$\underbrace{C_{14}H_8N_2O_2}_{\text{Anilo-urea.}} + 2\,(KO, HO) = \underbrace{C_{12}H_7N}_{\text{Aniline.}} + NH_3 + 2\,(KO, CO_2).$$

Anilo-urea dissolves in concentrated sulphuric acid without decomposition; on heating the solution, a brisk evolution of pure carbonic acid takes place, the residue contains sulphate of ammonia, and the conjugated sulphuric acid which M. Gerhardt* obtained by the action of sulphuric acid on various anilides. The brown residuary liquid solidifies, on the addition of water, to a slightly reddish crystalline mass, which may be purified by solution in boiling water and treatment with animal charcoal. A slowly cooling solution deposits splendid rhombic crystals, of considerable size and remarkable lustre.

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* Journal de Pharmacie, 3 Sér. t. x. p. 1.

The following equation illustrates this transposition:

$$\underbrace{C_{14}\,H_8\,N_2\,O_2}_{\text{Anilo-urea.}} + 3\,H\,SO_4 = \underbrace{C_{12}\,H_7\,N\,S_2\,O_6}_{\text{Sulphanilic acid.}} + 2\,CO_2 + NH_4\,SO_4.$$

Although the behaviour of the acid, produced in this reaction, left no doubt respecting its identity with anil-sulphuric acid, a sulphur determination was nevertheless made.

0·4268 grm. of the acid, burned with a mixture of carbonate and nitrate of potash, gave:

0·5835 grm. of sulphate of baryta corresponding to 18·75 per cent. of sulphur.

The formula:

$$C_{12}\,H_7\,N\,S_2\,O_6$$

requires the following values:

	Theory.		Experiment.
12 equiv. of Carbon . . .	72	41·62	—
7 " " Hydrogen . . .	7	4·04	—
1 " " Nitrogen . . .	14	8·09	—
2 " " Sulphur . . .	32	18·49	18·75*
6 " " Oxygen . . .	48	27·76	—
1 " " Sulphanilic acid . .	173	100·00	

The method by means of which I first obtained anilo-urea, viz.: the action of hydrated cyanic acid on aniline, very naturally suggested the idea that this compound must be considered as an analogue of urea; as urea containing the elements $C_{12}\,H_4$.

Urea . . . $N\,H_3\,H\,C_2\,N\,O_2$
Anilo-urea . . $(C_{12}\,H_4)\,N\,H_3\,H\,C_2\,N\,O_2$,

and hence the name under which I have described it.

This mode of regarding it is, however, not supported by the chemical deportment of the compound; in anilo-urea we no longer find a remnant of basic properties. I have vainly endeavoured to combine it with acids, in order to produce compounds analogous to nitrate or oxalate of urea. The presence of these acids does not increase the solubility of the aniline compound in water, and the crystals deposited on cooling retain no acid. My attempts to form a platinum-salt have likewise been unsuccessful.

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* The slight excess of sulphur arose from the presence of a trace of sulphate in the carbonate used.

The formula of anilo-urea admits, however, of another interpretation, which is strikingly supported by experimental evidence. The following equation:

$$C_{14}H_8N_2O_2 = NH_2, CO; C_{12}H_6N, CO,$$

shows that we may consider this substance, likewise, as a double compound of carbamide with its conjugated analogue. The existence of such double compounds is by no means isolated; in a Memoir on the metamorphosis of cyaniline, which I intend shortly to present to the Society, I shall have to describe a body of perfectly similar construction, viz. a compound of oxamide with oxanilide, corresponding in every respect to the preceding substance.

Carbamide-carbanilide . . $NH_2, CO; C_{12}H_6N, CO$
Oxamide-oxanilide . . . $NH_2, C_2O_2; C_{12}H_6N, C_2O_2$.

I was very curious to submit this idea to the test of experiment, and was fortunate enough to meet with a reaction, which leaves little doubt regarding the structure of anilo-urea, or carbamide-carbanilide, as the substance more properly should be called. I found that, when submitted to the action of heat, this compound actually splits into its proximate constituents; one of which, the carbanilide, is the principal product of the reaction, whilst the other, unable to exist at the temperature at which the separation takes place, undergoes a further metamorphosis, and can be recognized only in its derivatives.

In submitting anilo-uréa to the action of heat, the substance fuses without decomposition; on increasing, however, the temperature above the fusing point, torrents of ammonia are evolved, while the liquid in the retort solidifies to a crystalline mass, which again liquifies, and ultimately distils on a further elevation of the temperature. If the process be interrupted as soon as the evolution of ammonia ceases, and the solid begins to liquefy again, the residue in the retort consists of carbanilide and cyanuric acid. On treating this mixture with a large quantity of boiling water, the whole of the cyanuric acid, together with a small quantity of the other substance, is dissolved. In order to obtain the cyanuric acid, the aqueous solution is evaporated to dryness, and the residue extracted with alcohol, when carbanilide is dissolved, and the acid remains in a state of purity. The properties of cyanuric acid are so marked, that I have omitted to analyse the product; its comportment with solvents, and emitting also the well-known odour of cyanic acid when heated, appearing quite sufficient to obviate all chance of mistake.

The production of carbanilide, of ammonia, and of cyanuric acid in this reaction, admits of an easy explanation, if we recollect that carbamide is actually a submultiple of urea, which, as is well known, when submitted to dry distillation, is converted into ammonia and cyanuric acid.

Two equivalents of the compound contain the elements of two equivalents of carbanilide and one of urea:

$$2\,\underbrace{C_{14}\,H_8\,N_2\,O_2}_{\text{Carbamide-carbanilide.}} = 2\,\underbrace{C_{13}\,H_6\,NO}_{\text{Carbanilide.}} + \underbrace{C_2\,N_2\,H_4\,O_2}_{\text{Urea.}},$$

and the following equation exhibits the final results of the destruction of carbamide-carbanilide by heat:

$$6\,\underbrace{C_{14}\,H_8\,N_2\,O_2}_{\text{Carbamide-carbanilide.}} = 3\,NH_3 + 6\,\underbrace{C_{13}\,H_6\,NO}_{\text{Carbanilide.}} + \underbrace{H_3\,C_6\,N_3\,O_6}_{\text{Cyanuric acid.}}.$$

The substance which I have described in the preceding pages claims some interest, as the first conjugated amide which was discovered, and as the first member of a class of compounds, which has been enriched in so remarkable a manner by the investigations of MM. Gerhardt and Laurent.

CARBAMIDE-NITROCARBANILIDE.

Before passing to the description of carbanilide itself, I have to say a few words respecting a compound closely connected with the above double amide, the existence of which I have pointed out in my Memoir on melaniline.* When studying the action of chloride of cyanogen on nitraniline, I noticed that along with basic dinitromelaniline a neutral substance was formed, which separated in long yellow needles from the solution of the crude product of the reaction in boiling water.

Analysis, as might have been anticipated, proved this body to be the double amide: carbamide-nitrocarbanilide.

0·2706 grm. of substance gave:
0·4575 „ „ carbonic acid = 46·10 per cent of carbon, and
0·1015 „ „ water = 4·16 per cent of hydrogen.

The formula:

$$C_{14}\,H_7\,N_3\,O_6 = C_{14}\left\{\begin{matrix} H_7 \\ NO_4 \end{matrix}\right\}N_2\,O_2 = NH_2,\,CO\,;\ C_{12}\left\{\begin{matrix} H_5 \\ NO_4 \end{matrix}\right\}N,\,CO$$

requires the following values:

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* Journal of the Chemical Society, v. i. p. 305.

		Theory.		Experiment.
14 eq. of	Carbon	84	46·40	46·10
7 „	Hydrogen . . .	7	3·86	4·16
3 „	Nitrogen . . .	42	23·22	—
6 „	Oxygen . . .	48	26·52	—
1 „	Carbamide-nitrocarbanilide	181	100·00	

The formation of this compound will be evident from the following equation:

$$\underbrace{2\left(C_{12}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}N\right)}_{\text{Nitraniline.}}+C_2N\,Cl+2HO=\underbrace{C_{12}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}N,\,H\,Cl}_{\text{Hydrochlorate of nitraniline.}}$$

$$+\underbrace{C_{14}\left\{\begin{matrix}H_7\\N\ \ _4\end{matrix}\right\}N_2\,O_2.}_{\text{Carbamide-nitrocarbanilide.}}$$

An analogous iodine compound:

$$N\,H_2,\,CO;\,C_{12}\left\{\begin{matrix}H_5\\I\end{matrix}\right\}N,\,CO$$

is produced in the reaction of chloride of cyanogen on iodaniline along with diiodomelaniline. I have not analysed this compound.

CARBANILIDE.

This substance is but very slightly soluble in water; it dissolves more readily in alcohol and ether. The boiling alcoholic solution deposits, on cooling, beautiful satiny needles, which have frequently a reddish tint, from which they may be freed by recrystallization from alcohol with animal charcoal. It is inodorous, but emits, when heated, a suffocating odour resembling that of benzoic acid. It fuses at 205° C., and distils without alteration.

When speaking of the formation of anilo-urea, by passing the vapour of cyanic acid into aniline, I mentioned that care must be taken to avoid the liquid getting very hot, in order to prevent the formation of a secondary product. I need scarcely say that this secondary product is nothing but carbanilide, which may be easily separated from the accompanying compound.

The nature of carbanilide being once understood, other methods presented themselves for its preparation. The simplest plan appeared to be a reproduction of the circumstances under which carbamide was first obtained by M. Regnault. On exposing phosgene gas,* the interesting chloride of carbonic oxide, for the discovery of which we are indebted to Dr. John Davy, to the action of ammonia, the two gases solidified into a mixture of chloride of ammonium and carbamide.

$$2\,CO\,Cl + 2\,NH_3 = NH_4\,Cl + NH_2, CO.$$

This mixture admits of no complete separation of its two ingredients, both compounds exhibiting about the same behaviour with solvents, and it was by its reactions only, that M. Regnault succeeded in establishing its true nature.

The action of phosgene gas on aniline is perfectly analogous to that on ammonia, and the products of the reaction being easily separable, it affords a striking confirmation of M. Regnault's original explanation of the phenomenon. Aniline when introduced into an atmosphere of phosgene gas, solidifies at once into a crystalline mixture of carbanilide and hydrochlorate of aniline. The process is attended with a powerful evolution of heat.

$$2\,C_{12}\,H_7\,N + 2\,CO\,Cl = C_{12}\,H_7\,N, H\,Cl + C_{12}\,H_6\,N, CO.$$

It suffices to extract the crude product of the reaction with boiling water, when the hydrochlorate of aniline is dissolved, carbanilide remaining, which may be obtained in a state of purity by a single recrystallization from alcohol. This is certainly the simplest manner of obtaining carbanilide.†

The substances employed in the following analyses were partly obtained by this process (I. and II.), and partly by the action of cyanic acid on aniline (III. and V.) Combustion IV. was made with a product formed in the dry distillation of anilo-urea.

I. 0·4270 grm. of substance gave:
1·1400 „ „ carbonic acid, and
0·2200 „ „ water.

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* The name phosgene gas was originally framed by Dr. Davy, on account of the remarkable manner in which solar radiation promotes the combination of carbonic oxide with chlorine. The co-operation of sun-light, however, is not absolutely necessary; Dumas when studying the action of this compound on alcohol, ascertained that the combination likewise took place in reflected light, but much more slowly; I have lately found that phosgene gas may be readily obtained by passing carbonic oxide through boiling pentachloride of antimony, which by this treatment is reduced to the state of ter-chloride, and this reaction affords even a simple method of qualitatively ascertaining the presence of carbonic oxide in a mixture of gases; for the odour of phosgene gas is so peculiar, that it cannot be mistaken by a person who has once smelt it.

† Care must be taken, however, that the phosgene gas contain no free chlorine, which gives rise to the formation of a chlorinated compound, imparting a violet colour to the carbanilide, and can only be separated with great difficulty.

II. 0·3325 grm. of substance gave :
0·9020 „ „ carbonic acid, and
0·1771 „ „ water.
III. 0·3019 „ „ substance gave :
0·8182 „ „ carbonic acid, and
0·1610 „ „ water.
IV. 0·2534 „ „ substance gave :
0·6812 „ „ carbonic acid, and
0·1328 „ „ water.
V. 0·4160 „ „ substance gave :
0·3835 „ „ platinum.

Per-centage composition :

	I.	II.	III.	IV.	V.
Carbon . .	72·81	73·90	73·91	73·31	„
Hydrogen .	5·72	5·90	5·92	5·82	—
Nitrogen .	—	—	—	—	13·07

The formula :

$$C_{13} H_6 NO = C_{12} H_6 N, CO$$

requires the following values :

	Theory.		Mean of experiments
13 eq. of Carbon . .	78	73·58	73·48
6 „ Hydrogen . .	6	5·66	5·84
1 „ Nitrogen . .	14	13·01	13·07
1 „ Oxygen . .	8	7·75	—
1 „ Carbanilide . .	106	100·00	

The behaviour of carbanilide, with both concentrated acids and alkalies, agrees perfectly with the formula deduced by analysis. When boiled with concentrated sulphuric acid, this substance is converted into sulphanilic acid, pure carbonic acid being evolved.

$$\underbrace{C_{12} H_6 N, CO}_{\text{Carbanilide.}} + 2 HSO_4 = \underbrace{H SO_4 C_{12} H_6 N, SO_2,}_{\text{Sulphanilic acid.}} + CO_2.$$

Ebullition with concentrated potash solution, or fusion with solid hydrate of potash gives rise to the formation of carbonate of potash, while aniline distils over.

$$\underbrace{C_{12} H_6 N, CO}_{\text{Carbanilide.}} + HO, KO = \underbrace{C_{12} H_7 N_3}_{\text{Aniline.}} + KO, CO_2.$$

The same decomposition takes place, although less perfectly, even without the assistance of potash, if moist carbanilide is rapidly exposed to a high temperature, and hence the invariable presence of small quantities of carbonic acid and aniline among the products of the distillation of anilo-urea, if this substance has not been perfectly dried before the experiment.

The peculiar decomposition which anilo-urea exhibits under the influence of heat, induced me to study the phenomena attending the dry distillation of the corresponding sulphur compound, hydrosulphocyanate of aniline.

Hydrosulphocyanate of aniline is easily prepared by saturating free hydrosulphocyanic acid with an excess of aniline. The acid used in my experiments had been prepared by decomposing sulphocyanide of lead by hydrosulphuric acid. On evaporating the solution of hydrosulphocyanate of aniline, the compound separates in the form of deep red oily drops, which only gradually solidify into a crystalline mass. In repeated operations, I never succeeded in obtaining the salt perfectly colourless.

Action of heat on Hydrosulphocyanate of Aniline.

Dry hydrosulphocyanate of aniline, when exposed to the action of heat, fused at a very moderate temperature, and entered soon into a sort of ebullition, torrents of hydrosulphuric acid and of sulphide of ammonium being evolved, whilst on increasing the temperature, a colourless oily liquid distilled over, solidifying in the water of the receiver to a semi-solid crystalline mass. The residue in the retort is a slightly coloured resinous substance. In order to purify the crystalline compound, the whole distillate was subjected to another distillation. The liquid which now came over, separated into two distinct layers, of which the upper one contained a large quantity of hydrosulphuric acid and ammonia, whilst the lower one consisted of pure bisulphide of carbon. The products of the dry distillation of hydrosulphocyanate of aniline are, therefore, an *amorphous body* remaining in the retort, *ammonia*, *hydrosulphuric acid*, *bisulphide of carbon*, and a *crystalline substance*, which, as the subsequent analysis will prove, is a compound corresponding to carbanilide, in which the oxygen of the latter is replaced by an equivalent quantity of sulphur, a compound represented by the formula:

$$C_{12}\,H_6\,N,\,CS,$$

for which I propose the name of *Sulphocarbanilide*.

The decomposition which hydrosulphocyanate of aniline undergoes when submitted to destructive distillation is perfectly analogous to that of anilo-urea. Two equivalents of the hydrosulphocyanate split into two equivalents of sulphocarbanilide and one equivalent of sulphocyanide of ammonium, according to the equation:

$$2\,(\underbrace{C_{12}\,H_7\,N,\,H\,C_2\,N\,S}_{\text{Hydrosulphocyanate of aniline.}}) = 2\,(\underbrace{C_{12}\,H_6\,N,\,C\,S_2}_{\text{Sulphocarbanilide.}}) + \underbrace{NH_4,\,C_2\,N\,S_2}_{\text{Sulphocyanide of ammonium.}}.$$

Of course we cannot expect in a decomposition of this kind actually to separate the sulphocyanide of ammonium; this compound, like urea, being unable to exist at the temperature at which the decomposition takes place. But there is no difficulty in tracing it in its products of decomposition. From the experiments of Professor Liebig, we know that sulphocyanide of ammonium, when exposed to the action of heat, evolves ammonia, hydrosulphuric acid and bisulphide of carbon, whilst a residue remains, described by Liebig under the name of melam, splitting on the further application of heat again into mellon and ammonia. Now I have mentioned already that the distillate of hydrosulphocyanate of aniline, along with sulphocarbanilide, actually contains a large quantity of sulphide of ammonium and bisulphide of carbon. The residue in the retort seems to consist of mellon or melam, mixed with a small quantity of an aniline compound. The comparatively small scale in which I had to work, and the difficulty of purifying the mellon compounds, prevented me from entering upon a more minute investigation.

There is, however, but little doubt that the dry distillation of hydrosulphocyanate of aniline is illustrated by the above equation.

The preparation of sulphocarbanilide by the action of heat on the hydrosulphocyanate of aniline being rather a circuitous process, I tried to obtain the same compound by means of a different method. The ready production of carbanilide, by the action of phosgene gas on aniline, appeared to point out the course to be pursued. There was but little doubt that the compound in question would easily be formed by submitting aniline to the influence of a sulphur compound analogous to phosgene gas. A substance of this kind is known, but very imperfectly. In his remarkable paper on the conversion of bisulphide of carbon into the bichloride,* Dr. Kolbe states that the first product of the action of chlorine on bisulphide of carbon at high temperatures is the compound:

$$C\,S\,Cl.$$

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* Liebig's Annalen, Bd. XLV. S. 41.

The purification, however, of this substance appears to have been attended with so much difficulty, that a very satisfactory analysis of it is still wanting. Before recurring, therefore, to this difficult and still doubtful reaction, I tried whether sulphocarbanilide might not be formed by treating aniline with bisulphide of carbon.

Action of Bisulphide of Carbon on Analine.

Aniline and bisulphide of carbon may be mixed in every proportion. A mixture of this kind, when left for some hours, begins to evolve hydrosulphuric acid, and gradually solidifies into a scaly crystalline mass, which, after purification, is easily identified with sulphocarbanilide. The reaction is represented by the following equation:

$$\underbrace{C_{12}\,H_7\,N}_{\text{Aniline.}} + CS_2 = \underbrace{C_{12}\,H_6\,N,\,CS}_{\text{Sulphocarbanilide.}} + HS.$$

At the common temperature, weeks are required for the completion of the process; with the aid of heat, the conversion may be effected rapidly. The simplest plan is to fix a large Liebig's condensor vertically into a flask containing the mixture, which is gently heated for a day or two in a sand-bath over a gas flame. The presence of alcohol, I find, considerably accelerates the conversion. As soon as the evolution of hydrosulphuric acid ceases, the digestion is interrupted, and the crystals are freed from the remaining bisulphide of carbon by ebullition. One or two crystallizations from alcohol render them perfectly pure.

The action of bisulphide of carbon on aniline presents a most remarkable analogy with the decomposition occurring in a mixture of the same compound with ammonia. The experiments of Zeise have proved that an alcoholic solution of bisulphide of carbon, when saturated with ammonia, is gradually converted into the same ammonium compound, which Mr. Porret long ago obtained by saturating his hydrosulphocyanic acid with ammonia, viz. into sulphocyanide of ammonium. Now sulphocyanide of ammonium, although widely different in its chemical nature from sulphocarbanilide, nevertheless presents a striking analogy to this compound. Sulphocyanide of ammonium is a multiple of sulphocarbamide.

$$NH_4,\,C_2\,N\,S_2 = C_2\,H_4\,N_2\,S_2 = 2\,(NH_2,\,CS)$$

The modes of production of sulphocyanide of ammonium and sulphocarbanilide thus become perfectly parallel, as may be seen by the two following corresponding equations:

$$NH_3 + CS_2 = \underbrace{NH_2, CS}_{\text{Sulpho-cyanide of ammonium.}} + HS.$$

$$\underbrace{C_{12}H_7N}_{\text{Aniline.}} + CS_2 = \underbrace{C_{12}H_7N, CS}_{\text{Sulphocarbanilide.}} + HS.$$

For the following analyses, the compound was obtained in different preparations. The product employed in the first combustion was formed in the dry distillation of hydrosulphocyanate of aniline; the other analyses were made with the compound obtained by the action of bisulphide of carbon on aniline.

I. 0·2477 grm. of substance gave:
0·6219 „ „ carbonic acid, and
0·1204 „ „ water.
II. 0·2891 „ „ substance gave:
0·7253 „ „ carbonic acid, and
0·1365 „ „ water.
III. 0·3259 „ „ substance gave:
0·8120 „ „ carbonic acid, and
0·1542 „ „ water.
IV. 0·4593 grm. of substance gave:
54·5 C.C. of moist nitrogen at 21° C. and 0^m, 7596 Bar.

Of the following two sulphur determinations, the first was made by gradually deflagrating a mixture of the substance with nitrate of potash and carbonate of soda. A small quantity of the compound having been volatilized in this operation, a second experiment was made, in which the sulphocarbanilide was dissolved in fuming nitric acid, which converts it into a substitution-body, which is no longer volatile. The solution was evaporated to dryness, and the residue deflagrated in the usual manner with nitre and carbonate of soda.

V. 0·3809 grm. of substance gave:
0·3825 „ „ sulphate of baryta.
VI. 0·4985 „ „ substance gave:
0·5105 „ „ sulphate of baryta.

Per-centage composition:

	I.	II.	III.	IV.	V.	VI.
Carbon . .	68·47	68·42	67·95	—	—	—
Hydrogen . .	5·41	5·27	5·26	—	—	—
Nitrogen . .	—	—	—	12·63	—	—
Sulphur . .	—	—	—	—	13·67	14·04

the mean of which closely agrees with the values of the formula:

$$C_{13}\,H_6\,N\,S,$$

as may be seen from the following table:

	Theory.		Mean.
13 equiv. of Carbon	78	68·42	68·28
6 „ „ Hydrogen	6	5·24	5·28
1 „ „ Nitrogen	14	12·29	12·63
1 „ „ Sulphur	16	14·03	13·85
1 „ „ Sulphocarbanilide	114	100·00	100·04

Sulphocarbanilide is but slightly soluble in water, it dissolves more readily in alcohol and ether, the boiling solutions deposit the compound, on cooling, in beautifully iridescent plates of remarkable lustre. Sulphocarbanilide is distinguished by its bitter taste, it is in fact one of the bitterest substances I ever met with. It has a peculiar smell, which becomes more perceptible on heating. It fuses at 140° C. (284° F.) and distils without decomposition.

Dilute acids and alkalies have no action on sulphocarbanilide; when concentrated, they decompose the compound, and these decompositions are analogous to the corresponding changes of carbanilide. Sulphocarbanilide dissolves in concentrated sulphuric acid; on gently heating this substance a brisk effervescence takes place, carbonic and sulphurous acids being evolved; the remaining solution solidifies on the addition of water into a crystalline mass of sulphanilic acid.

The equation:

$$\underbrace{C_{12}\,H_6\,N,\,CS}_{\text{Sulphocarbanilide.}} + 2\,H\,SO_4 = \underbrace{C_{12}\,H_7\,N\,S_2\,O_6}_{\text{Sulphanilic acid.}} + CO_2 + HS$$

illustrates the decomposition; it is evident that the hydrosulphuric acid of this equation, when coming into contact with concentrated sulphuric acid, is decomposed with the formation of sulphurous acid and the deposition of sulphur. In fact, on adding to the liquid a sufficient quantity of water to dissolve the sulphanilic acid, a muddy solution is obtained, from which a large quantity of free sulphur is deposited:

$$HS + H\,SO_4 = 2\,HO + S + SO_2.$$

On fusing sulphocarbanilide with solid potash, pure aniline distils, a mixture of carbonate of potash, and sulphide of potassium remaining in the retort:

$$\underbrace{C_{12}H_6N,}_{\text{Sulphocarbanilide.}} CS + 2(HO, KO) = \underbrace{C_{12}H_7}_{\text{Aniline.}} N + KS + KO, CO_2 + HO.$$

If instead of solid potash, an alcoholic solution of that base be employed, the reaction is considerably modified. In this case the oxygen is simply exchanged for sulphur, sulphide of potassium and carbanilide being formed, which crystallizes, on cooling, from the alkaline solution in long beautiful needles.

$$\underbrace{C_{12}H_6N, CS}_{\text{Sulphocarbanilide.}} + KO = KS + \underbrace{C_{12}H_6N, CO}_{\text{Carbanilide.}}.$$

The alcoholic solution of potash may be advantageously replaced by protoxide of mercury. Indeed, on boiling an alcoholic solution of sulphocarbanilide with protoxide of mercury, the red colour of the oxide at once disappears, black protosulphide being deposited, whilst carbanilide crystallizes from the solution.

The rapid action of protoxide of mercury on the sulphur compound, induced me to examine its behaviour with chloride, bromide, iodide, and cyanide of mercury, in order to form the corresponding chlorine, bromine, iodine, and cyanogen compounds. These salts, however, are without action on sulphocarbanilide.

The following table embraces the compounds, the analysis of which I have communicated on the preceding pages.

Carbamide-carbanilide .	$NH_2, CO; C_{12}\ H_6\ N, CO$
Carbamide-nitrocarbanilide .	$NH_2, CO; C_{12}\left\{\begin{matrix}H_5\\NO_4\end{matrix}\right\}N, CO$
Carbanilide . . .	$C_{12}\ H_6\ N, CO$
Sulphocarbanilide . .	$C_{12}\ H_6\ N, CS$

Jan. 15, 1849.

Colonel Philip Yorke in the Chair.

The following presents were announced :—" On the Phosphoric Strata of the Chalk Formation," by Messrs. J. M. Paine and J. T. Way, from the authors ; " Report on the Analysis of the Ashes of Plants," Part III., by Messrs. J. T. Way and G. Ogston, from the authors.

The following communications were read :

V.—*On the Salts of Selenious Acid. By* DR. SHERIDAN MUSPRATT, *Professor to the Liverpool College of Chemistry.*

PRELIMINARY REMARKS.

I undertook the investigation of the salts of selenious acid, with the view of ascertaining whether they were analogous to those of sulphurous acid.

Mitscherlich has remarked, that the selenic and sulphuric acids are not only analogous in composition and in many of their properties, but that the similarity runs through their salts, which resemble one another, in chemical comportment, constitution, and form. We might infer from this, that the selenites and sulphites would be isomorphous, sulphur and selenium being so analogous. In a former paper,* I mentioned the great similarity between carbon and sulphur, which also extends to the carbonates and sulphites. For nearly every carbonate, I obtained a corresponding sulphite. The formulæ of the three acids are appended, in order to show their striking analogies :

Carbonic acid	CO_2
Sulphurous acid	SO_2
Selenious acid	SeO_2.

We see, on referring to the above, that they all contain the same amount of oxygen, *i. e.* 2 equivs of oxygen united to either carbon, sulphur, or selenium.

Although I proved the isomorphism with regard to the first two, my results with selenious acid are only in a few cases similar to those with sulphurous acid. One of the great causes of this may be the persistency of the former, and the instability of the latter. There were numerous difficulties to contend with in the preparation and analysis of the salts of this acid, as will be hereafter mentioned.

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* Liebig's Annalen der Chemie, Band L. p. 259.

PREPARATION OF THE ACID.

Selenium was dissolved in pure, fuming, nitric acid, and the solution evaporated on a sand-bath to dryness. The nitric acid, when added, caused a most violent action, large quantities of nitrous fumes being disengaged. The residue was a white powder, possessing a sour and styptic taste, which, heated on a sand-bath, afforded as a sublimate, most magnificent silvery-looking, very long, four-sided needles of selenious acid.

This acid is also formed by acting upon selenium with *aqua regia.* The former method, however, is preferable.

$$9\ \mathrm{Se} + 6\ \mathrm{NO_5} = 9\ \mathrm{SeO_2} + 6\ \mathrm{NO_2}.$$

GENERAL PROPERTIES OF THE ACID AND SALTS.

Berzelius has made allusion to many of the following properties of selenious acid and its salts. In some cases, this illustrious Swede has not been sufficiently specific, owing, no doubt, to the enormous number of facts he had to contend with in other departments of the Science. It is stated in Turner's Chemistry,* *"when sulphurous acid is added to a solution of selenious acid, pure selenium is thrown down."* In the cold, I could not obtain this reaction, but when the two acids are mixed together *and boiled,* a vermilion-coloured precipitate, selenium, separates. Strong hydrosulphuric acid decomposes selenious acid immediately in the cold, an orange-yellow powder subsiding; a sulphide of selenium. The preceding decompositions may be represented as follows:

$$\mathrm{SeO_2} + 2\ \mathrm{SO_2} = \mathrm{Se} + 2\ \mathrm{SO_3}$$
$$\mathrm{SeO_2} + 2\ \mathrm{HS} = \mathrm{SeS_2} + 2\ \mathrm{HO}.$$

Hydrochloric acid has not the slightest effect upon selenious acid.

Selenious acid is reduced when heated on charcoal before the blow-pipe, the selenium imparting a beautiful blue colour to the flame. The fumes evolved are yellowish, and have the smell of decayed horseradish; a most characteristic test for the acid. The smell is so persistent, that for days my clothes have retained it. This acid very seldom forms basic salts, and then only with those metallic oxides which readily afford them with other acids.

It easily produces a basic salt with oxide of copper, in this respect materially differing from sulphurous acid.

On passing sulphurous acid into water, holding oxide of copper in suspension, a reduction takes place, the sub-oxide of copper being formed.

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* Eighth Edition, p. 265.

$$2\ CuO + SO_2 = SO_3 + Cu_2\ O.$$

When a selenite is heated in contact with any organic matter, reduction immediately occurs; great care has, therefore, to be exercised in the preparation of the salts, not to allow any of the filtering paper to adhere to them.

Charcoal reduces the salts immediately at a high temperature. If charcoal is fused with selenite of soda, selenide of sodium and carbonic acid are obtained.

$$+ 2\ (NaO,\ SeO_2) + 3\ C = 2\ (Na\ Se) + 3\ CO_2.$$

Chloride of ammonium distilled with a selenite affords selenium, which condenses in the neck of the retort. The decomposition may be exhibited by the following equation:

$$3\ (NaO,SeO_2) + 3\ (NH_4Cl) =$$
$$3\ Se + 2\ N + NH_4O + 3\ NaCl + 8\ HO.$$

Three equivalents of selenite of soda and 3 equivalents of chloride of ammonium contain the elements of 3 equivalents of selenium, 2 of nitrogen, 3 of chloride of sodium, 8 of water, and 1 equivalent of oxide of ammonium. Selenious acid liquefies on exposure to the air.

The neutral salts of selenious acid, with potash, soda and ammonia, have a very caustic taste, and react alkaline. They are extremely soluble in water.

When aqueous selenious acid is neutralized by the alkalies, and the liquid is treated with alcohol, under certain circumstances, an oily substance separates; this, when kept for a long time, becomes crystalline.

Selenites of the alkalies are most difficult to prepare. They are remarkably deliquescent, and liable to undergo decomposition, unless carefully dried over sulphuric acid. The neutral salts taste and react alkaline. They dissolve with a slight reddish colour, owing to a trace of reduced selenium; a remarkable circumstance.

Selenious acid is extremely stable. When the crystals of the acid are exposed to the air for weeks, although they liquefy, still I could not detect in them any *selenic* acid. How different is the case with sulphurous acid, which cannot be exposed to the air for an hour without a portion being converted into sulphuric acid. Selenious acid, according to Berzelius, has a great tendency to form acid salts, even in the relation of *four* of acid to one of base. I obtained a syrupy mass in one instance, which, when analysed, agreed with the statement above. I could not, however, obtain any quadracid salt in a perfectly dry state. My intention in the present paper is to embrace all that is known respecting the selenites, so that future investigators may have a full reference.

I find, as did Berzelius, when an alkali is treated with selenious acid, until the liquid reacts neither acid nor alkaline, that on evaporation, crystals of a bisalt are deposited; a neutral salt remaining in solution.

Rose has remarked, that hyposulphite of ammonia only partially precipitates selenium in the cold; more is precipitated by boiling, and still more on the addition of hydrochloric acid. In the cold, the decomposition takes place extremely slowly, if at all; on boiling, however, bisulphide of selenium is deposited—a large quantity is precipitated in the presence of hydrochloric acid:

$$SeO_2 + 2\ (S_2\ O_2) = SeS_2 + 2\ SO_3.$$

When *aqua regia* is added to the bisulphide of selenium, it is immediately decomposed.

Boracic, phosphoric, and sulphuric acids, expel selenious acid from its compounds at a high temperature. I employed sulphuric acid for this purpose in analysing the salts.

Hydrochloric acid *has not the slightest effect,* even when boiled with selenious acid; selenic acid, however, is reduced by it to the state of selenious acid:

$$SeO_3 + HCl, = SeO_2 + HO + Cl.$$

Many of the salts of selenious acid lose their acid when heated; others part with only a portion, and some do not evolve any, as will be seen under the description of the various salts.

SELENITES OF POTASH.

The neutral selenite is obtained by saturating carbonate of potash with selenious acid, and evaporating quickly to dryness. I could not obtain the salt for a long time in a fit state for analysis, owing to there always being an excess of selenious acid. A definite salt is also extremely difficult to prepare, on account of traces of selenium separating. Selenite of potash is remarkably soluble in water. It is almost insoluble in alcohol; but, strange to say, I could not precipitate it from its aqueous solution in a crystalline state by alcohol. An oily substance always appeared. It possesses a disagreeable taste, is very alkaline to test-paper, and deliquescent; on which account, great care has to be exercised in weighing the salt.

0·251 grms. salt gave:
0·210 „ sulphate of potash =
0·113 „ potash,

leading to the formula:

$$KO, SeO_2.$$

Centesimally represented:

		Theory.	Exp.
1 eq. of selenious acid .	56	53·85	
1 „ of potash . . .	48	46·15	45·02
	104	100·00	

Biselenite of potash gives satiny-looking crystals. It is obtained by decomposing carbonate of potash with an excess of selenious acid, and allowing the solution to evaporate over sulphuric acid; or by precipitating the solution with alcohol, in which menstruum the biselinite is only slightly soluble. The difficulty attending the preparation of this salt is very great. Too much selenious acid must not be added to the carbonate of potash, or crystallization will never take place. When the liquid is made slightly acid, the crystals are not more than two days in forming.

Alcohol nearly always precipitates an oily liquid from the slightly acid aqueous solution, which speedily, however, becomes crystalline. The crystals, dried for eight days over sulphuric acid, were analysed:

0·894 grm. salt gave
8·351 „ sulphate of potash,

leading to the formula:

$$KO, SeO_2, + HO, SeO_2$$

		Theory.	Experiment.
2 eqs. of selenious acid .	112	66·272	
1 „ of potash . .	48	28·402	28·05
1 „ of water . .	9	5·326	
	169	100·000	

Biselenite of potash is analogous to the bisulphite of the same base:

$$KO, SeO_2, + HO, SeO_2$$
$$KO, SeO_2, + HO, SO_2.$$

On heating the biselenite in a dry test-tube, water first passes off, and is followed by selenious acid. The whole mass then fuses to a red fluid, which ultimately becomes colourless, and on cooling, solidifies into a fine crystalline mass, soluble in water, and precipitable by alcohol. It is the neutral selenite of potash.

A most disagreeable odour of horseradish is evolved as the liquid reddens. The quadriselenite of potassa described by Berzelius—

$$KO, 4\ SeO_2, \text{ or}$$
$$KO, SeO_2, +3\ (HO, SeO_2)\ ?$$

is not attainable in a fit state for analysis. This salt is styptic to the taste, and when heated, evolves most stifling fumes. It is in a high degree deliquescent.

SELENITES OF SODA.

When carbonate of soda, saturated with selenious acid, is allowed to evaporate under a bell-jar, the syrupy mass becomes filled with radiated crystals; which will be subsequently described. The liquid gives a neutral salt on the addition of alcohol. This salt, not being deliquescent, is more easily obtained than the salt of potash. It was desiccated between folds of bibulous paper, and then left over sulphuric acid for some days:

0·400 grms. of salt gave:
0·320 „ sulphate of soda=
0·142 „ soda,

agreeing with the formula:

$$NaO, SeO_2.$$

		Theory.	Experiment.
1 eq. selenious acid . .	56	63·63	
1 „ soda. . . .	32	36·37	35·50
	88	100·00	

The above corresponds with the formulæ for dry carbonate and sulphite of soda:

$$NaO, CO_2$$
$$NaO, SO_2$$
$$NaO, SeO_2.$$

Selenite of soda, heated in a test-tube, gives off a mere trace of water, the salt fuses, but does not suffer decomposition. From the aqueous solution, I could not succeed in obtaining the neutral salt with water of crystallization. Biselenite of soda forms acicular crystals.

0·2410 grms. of salt gave:
0·0251 „ water.

The annexed formula is deduced from the above:

$$NaO, SeO_2, +\ HO, SeO_2 + 2\ aq.$$

Represented in 100 parts:

		Theory.	Experiment.
1 eq. of selenite of soda .	88	51·46	
1 „ „ „ „ water .	65	38·02	
2 eqs. „ water . . .	18	10·52	10·41
	171	100·00	

The biselenite does not suffer decomposition except at a very high temperature. On a sand-bath *it parts only with its water of crystallization.* At a red heat, it fuses into a yellowish liquid, water passing off with selenious acid; the neutral salt remains as a fine silvery-white, crystalline mass.

QUADRISELENITE OF SODA.

I dissolved biselenite of soda in selenious acid, and put aside the liquid to evaporate spontaneously. After some days, needle-like crystals separated, which were not very deliquescent. When dried over sulphuric acid and analysed:

I. { 0·862 grm. salt gave:
0·241 „ sulphate of soda =
0·107 „ soda.

II. { 0·804 grm. salt gave:
0·210 „ sulphate of soda =
0·093 „ soda.

The preceding results agree closely with the following singular formula:

$$NaO, SeO_2 + 3 (HO\ SeO_2) + aq.$$

		Theory.	Experiment.	
			I.	II.
4 eq. selenious acid .	224	76·712		
1 „ soda. . .	32	10·958		
4 „ water . .	36	12·33	12·41	11·56
	292	100·000		

This salt fuses readily into a yellowish-red liquid, evolving selenious acid and water, while selenite and traces of selenate of soda remain.

SELENITES OF AMMONIA.

These salts are extremely difficult to prepare. I could not obtain a selenite of ammonia from an aqueous solution in a fit state for analysis, After a number of vain attempts, alcohol was resorted to. Selenious acid, dissolved in alcohol, and treated with ammoniacal gas, afforded magnificent shining crystals, which, however, were deliquescent. This salt is also obtained by dissolving selenious acid in strong aqueous ammonia, and precipitating by alcohol. When a drop of strong ammonia is added to crystallized selenious acid, combination immediately takes place, great heat is evolved, and particles of selenium sometimes separate.

Selenite of ammonia is strongly alkaline to the taste, and smells *slightly of ammonia.* It is very soluble in water—perfectly insoluble in ether:

0·2505 grm. salt gave:	0·25050
0·3100 „ platinum =	0·31000
0·08141 „ oxide of ammonium,	0·08141

agreeing with the formula:

$$NH_4O, SeO_2.$$

		Theory.	Found.
1 eq. selenious acid . .	56	68·30	
1 „ oxide of ammonium .	26	31·70	32·49
	82	100·00	

Selenite of ammonia, heated in a dry test-tube, gives off, first water and ammonia, then water and nitrogen, while an acid salt condenses in the upper part of the tube; lastly, large quantities of selenium sublime. The decomposition is represented in its several stages by the annexed equation.

$$5\ (NH_4O,\ SeO_2)\ =$$
$$HO,\ +\ 2\ NH_4O,\ +\ 7\ HO,\ +\ 2\ N,\ +NH_4O{\cdot}2\ Se{\cdot}O_2,\ +\ 3\ Se.$$

Biselenite of ammonia does not deliquesce, it is composed, according to Berzelius, as follows:—

$$NH_4O,\ 2\ SeO_2.$$

Its formula is probably:

$$NH_4O,\ SeO_2\ +\ HO,\ SeO_2\ ?$$

Quadriselenite of ammonia is not crystallizable.

SELENITES OF BARYTA.

Selenious acid produces no precipitate with solutions of baryta. By this reaction it is at once distinguished from sulphurous acid. When neutral selenite of potash is added to nitrate of baryta, decomposition takes place, selenite of baryta is deposited in fine shining plumose crystals, which are soluble in selenious, nitric, and hydrochloric acids. From the acid solution, the baryta is immediately precipitated by sulphuric acid.

0·308 grm. salt gave
0·271 „ sulphate of baryta =
0·177 „ baryta.

Numbers agreeing with the formula:

$$BaO, SeO_2$$

Centesimally represented:

		Theory.	Berzelius.	Experiment.
1 equiv. selenious acid .	56	42·42	42·07	—
1 „ barytes	76	57·58	57·93	57·46
	132	100·00	100·00	

Biselenite of baryta is obtained by expelling the carbonic acid from the carbonate of baryta with selenious acid, and allowing the liquid to evaporate spontaneously. It is with difficulty dissolved in water. Ammonia, when added to it, precipitates the neutral salt. At a high temperature, the biselenite evolves water and white fumes of selenious acid.

SELENITES OF STRONTIA.

These salts are obtained in a similar manner to those of baryta. Selenite of strontia is a white insoluble powder. It does not contain water. The following is its formula:

$$SrO, SeO_2.$$

Biselenite of strontia does not crystallize. Its behaviour, when heated, corresponds to the acid salt of baryta. It is slightly soluble in water.

SELENITES OF LIME.

Carbonate of lime with selenious acid yields gritty crystals of selenite of lime. Berzelius has remarked the singular effect of this salt upon glass. At a red heat the tube is sometimes eaten through. A most remarkable characteristic of this and a few other of the salts of selenious acid.

Formula—CaO, SeO_2

The selenite of lime dissolves in selenious acid, giving a biselenite, which is very persistent in the air.

SELENITES OF MAGNESIA.

When all the carbonic acid is expelled from carbonate of magnesia by selenious acid, there remains a heavy neutral crystalline salt, which dissolves in boiling water, and crystallizes from it in rhombic prisms. Selenite of magnesia, heated over the lamp, gives off only its water of crystallization. It fuses at a red heat in a glass tube, corroding and passing through it like the selenite of lime.

0·209 grm. of salt, strongly heated, gave:
0·056 „ „ water.

Formula—$MgO, SeO_2 + 3$ aq.

		Theory.	Experiment.
1 eq. Selenious acid . .	56	54·36	—
1 „ Magnesia . .	20	19·42	—
3 „ Water	27	26·22	26·79
	103	100·00	

This salt is isomorphous with the sulphite and carbonate of the same base:

$MgO, SeO_2 + 3$ aq.
$MgO, SO_2 + 3$ aq.
$MgO, CO_2 + 3$ aq.

Selenite of magnesia dissolves in selenious acid, yielding a biselenite, precipitable in an unctuous state by alcohol. It is extremely deliquescent.

SELENITES OF ALUMINA.

Alum is not precipitated by selenious acid. A selenite of an alkali, however, precipitates a selenite of alumina. Great care must be taken that the precipitant is neutral. Selenite of alumina is amorphous. When heated it gives off water, and lastly, all its acid.

0·197 grm. of dry salt gave:
0·150 „ selenious acid, and
0·046 „ alumina.

		Theory.	Experiment.
3 eqs. Selenious acid	168	76·36	76·14
1 „ Alumina	52	23·64	23·36
Loss	—	—	·50
	220	100·00	100·00

I also determined the water in the salt dried over sulphuric acid.

0·112 grm. of salt gave:
0·012 „ „ water.

Centesimally represented:

		Theory.	Experiment.
3 eqs. Selenious acid	168	68·01	—
1 „ Alumina	52	21·17	—
3 „ Water	17	10·82	10·71
	247	100·00	

Formula—$Al_2 O_3, 3 SeO_2 + 3$ aq.

The composition of the selenite of alumina is greatly different from the sulphite, as represented by the formula:

$Al_2 O_3, SO_2 + 4$ aq.

Biselenite of alumina is obtained when the above salt is dissolved in selenious acid. It is transparent and gummy to the feel. According to Berzelius, it contains six equivalents of acid.

$Al_2 O_3, 6 SeO_2$

In all probability its composition is the following:

$Al_2 O_3, 3 SeO_2 + 3 (HO SeO_2)$?

SELENITES OF GLUCINA.

This selenite is, in every way, analogous to that of alumina, the biselenite is extremely soluble, and does not crystallize.

SELENITE OF CHROMIUM.

This salt is obtained by decomposing the chloride of chromium by selenite of ammonia. It is a fine green amorphous powder.

0·3006 grm. salt gave:
0·0980 „ oxide of chromium.

Formula—$Cr_2 O_3, 3 SeO_2$

		Theory.	Experiment.
3 eqs. Selenious acid . . .	168	67·74	—
1 „ Oxide of chromium . .	80	32·26	32·60
	248	100·00	

Selenite of chromium dissolves in selenious acid, giving on evaporation a green varnish.

SELENITES OF IRON.

Metallic iron is not dissolved by selenious acid. Selenium is deposited on its surface in red flakes. Selenite of iron precipitates as a white powder from a mixture of an alkaline selenite and sulphate of iron. It becomes darker on exposure to the air, and after some time partakes of a yellow colour, owing to the formation of some sesquioxide. When the white precipitate is dissolved in hydrochloric acid, a portion of selenium separates, and sesquichloride of iron with selenious acid remain in solution.

$$4\ (FeO,\ SeO_2) + 6\ HCl = \\ Se, + 2\ (Fe_2\ Cl_3,) + 6\ HO, + 3\ SeO_2.$$

Biselenite of iron is formed by dissolving the selenite in selenious acid. When the liquid is boiled, a brown powder separates, containing selenite of the sesquioxide of iron with selenium.

Selenite of the sesquioxide of iron falls as a white powder when selenite of ammonia is added to sesquichloride of iron. It is yellowish when dry, and loses water, in the heat, becoming darker, and as the temperature augments, all its acid volatilizes.

0·1015 grm. salt gave :
0·0720 „ selenious acid and water,

which agrees sufficiently with the formula :

$$Fe_2\ O_3,\ 3\ SeO_2 + 4\ aq.$$

Calculated on 100 parts :

		Theory.	Experiment.
1 eq. Sesquioxide of iron	80	28·16	—
3 „ Selenious acid	168	59·15	70·94
4 „ Water	36	12·69	
	284	100·00	

According to Berzelius, the bisalt is formed when iron is dissolved in a hot mixture of nitric and selenious acids. The salt is deposited, on cooling, in green plates, which contain water of crystallization. They are not soluble in water, but dissolve readily in hydrochloric acid, imparting a yellowish colour :

The formula for the salt, is :

$$Fe_2\ O_3,\ 3\ SeO_2 + 3\ (HO\ SeO_2)\ ?$$

A basic salt is obtained when either of the two preceding salts is digested in ammonia, the formula for which is :

$$2\ Fe_2\ O_3,\ 3\ SeO_2.$$

SELENITES OF MANGANESE.

I dissolved carbonate of manganese in selenious acid, and obtained a white gritty powder, which readily fused to a dark liquid in a glass tube, corroding it more even than the magnesia-salt. Selenious acid sublimed, and sesquioxide of manganese, with some selenium, remained:

0·200 grm. salt fused with nitrate of potash, gave
0·250 grm. selenate of baryta =
0·100 grm. selenious acid.

The formula is therefore

$$MnO, SeO_2 + 2\ aq.$$

Represented in 100 parts.

		Theory.	Experiment.
1 eq. selenious acid	56	50·90	50·00
1 „ oxide of manganese .	36	32·73	—
2 „ water	18	16·37	—
	110	100·00	—

This salt agrees in composition with the carbonate and sulphite of manganese:

$$MnO, SeO_2 + 2\ aq.$$
$$MnO, CO_2 + 2\ aq.$$
$$MnO, SO_2 + 2\ aq.$$

Selenite of manganese is insoluble in water, it forms a colourless solution in cold, and a pink solution in hot, hydrochloric acid. With selenious acid, it yields a soluble biselenite.

SELENITES OF NICKEL.

The neutral salt falls as a greenish powder when selenite of potassa is added to sulphate of nickel. In its dry state the salt is white. Dried over sulphuric acid:

0·207 grm. salt gave:
0·019 „ water.

Numbers corresponding to the formula:

$$NiO, SeO_2 + aq.$$

Calculated on 100 parts.

		Theory.	Experiment.
1 eq. selenious acid	56	54·36	—
1 „ oxide of nickel . .	38	36·89	—
1 „ water	9	8·75	9·17
	103	100·00	

Selenite of nickel dissolves in selenious acid with a greenish colour. The liquid, on evaporation, yields a gummy acid salt.

SELENITES OF COBALT.

The neutral salt procured by double decomposition is an insoluble rose-coloured powder. In all probability its composition is similar to the nickel compound. Carbonate of cobalt dissolves in selenious acid with a fine pink colour. The liquid, on evaporation, yields a magnificent transparent violet-coloured gum—an acid salt. This resinous substance, when heated on a sand-bath, gives off selenious acid, which condenses on the sides of the vessel in beautiful white needles.

SELENITES OF ZINC.

Selenious acid does not precipitate salts of zinc; in combination with an alkali, however, it gives, when added to sulphate of zinc, white crystalline grains of selenite of zinc. When this salt is heated, it evolves water, but as the temperature augments, the salt fuses to a yellow liquid, which, on cooling, presents a fine crystalline striated appearance. At a white heat the mass gives off selenious acid, leaving a basic salt:

0·0522 grm. salt gave :
0·0087 „ water.

From which the following formula is deduced:

$$ZnO, SeO_2 + 2\ aq.$$

Represented in 100 parts:

		Theory.	Experiment.
1 eq. selenious acid . . .	56	49·12	—
1 „ oxide of zinc . . .	40	35·08	—
2 „ water	18	15·80	16·66
	114	100·00	

This salt corresponds to the sulphite of zinc:

$$ZnO, SeO_2 + 2\ aq.$$
$$ZnO, SO_2 + 2\ aq.$$

Selenite of zinc dissolves in selenious acid, yielding an uncrystallizable biselenite.

SELENITES OF CADMIUM.

Selenious acid does not precipitate salts of cadmium. Selenite of ammonia gives, with chloride of cadmium, a white argillaceous looking precipitate. This becomes orange on exposure to the air. Selenite of cadmium contains no water. It is soluble in selenious acid. When heated in a test-tube, it gives a sublimate of a yellowish-red colour.

SELENITES OF COPPER.

When biselenite of ammonia is added to a hot solution of sulphate of copper, a dirty greenish-yellow precipitate falls, which after some time becomes a fine bluish-green crystalline salt. This compound, dried over sulphuric acid, acquires a beautiful bright blue colour.

I. 0·5260 grm. salt gave
0·2133 „ oxide of copper.
0·0526 „ salt gave
0·0018 „ water,

and

II. 0·0534 grm. salt gave
0·0017 „ water.

The above results agree very closely with the formula:

$$3\ (CuO,\ SeO_2) + aq.$$

Centesimally represented:

	Theory.		Experiment. I.	Experiment. II.
3 eq. selenious acid	168	56·56	—	—
3 „ oxide of copper . .	120	40·40	40·55	—
1 „ water	9	3·04	3·42	3·18
	297	100·00		

This salt does not dissolve in aqueous selenious acid. At a high temperature it first becomes brown, lastly black, parting with all its acid. A green basic selenite of copper is formed when selenite of ammonia is added to sulphate of copper. It is insoluble in water, but dissolves in ammonia. Freshly precipitated suboxide of copper combines with selenious acid, producing a whitish salt. The formula for which is:

$$Cu_2\ O,\ SeO_2 + aq.\ ?$$

SELENITES OF LEAD.

Selenious acid gives a white curdy precipitate with acetate of lead, which is slightly soluble in water. The precipitate contains no water. It is with difficulty decomposed by sulphuric acid. When heated very strongly, it fuses into a yellowish fluid, selenious acid sublimes, and a basic salt remains. The formula for this salt is:

$$PbO, SeO_2.$$

SELENITE OF SILVER.

Berzelius analysed the selenite of silver. It is thrown down in the form of a white powder on the addition of aqueous selenious acid to nitrate of silver; it is fusible, and at a red heat loses its acid and all its oxygen, leaving metallic silver. When perfectly dry, it is not blackened on exposure to light. It is slightly dissolved by cold, more by boiling water, is easily soluble in hot nitric acid, from which it crystallizes in needles. The salt is obtained perfectly pure in this way. The formula for the salt is:

$$AgO, SeO_2.$$

SELENITES OF MERCURY.

The selenite of the suboxide of mercury is obtained by adding selenious acid to a solution of subnitrate of mercury; also by double decomposition. It is a white powder, insoluble in water. Heated in a tube, it blackens, water is liberated, and a yellow powder sublimes. When the latter is heated, it fuses into beautiful red globules, which become of an orange colour on cooling; in fact a series of cameleon-like changes occur with this salt. As the tube gradually cools, splendent golden yellow crystals become visible. Caustic potash takes the selenious acid from the selenite. It dissolves in hydrochloric acid, giving chloride of mercury, water, selenious acid, and selenium.

$$2\,(Hg_2\,O,\,SeO_2) + 4\,HCl =$$
$$4\,(Hg\,Cl) + 4\,HO + SeO_2 + Se.$$

Selenite of the protoxide of mercury is a white insoluble powder. The bisalt, according to Berzelius, is obtained by digesting the oxide of mercury for a long time in selenious acid. On filtering and evaporating the filtrate, prismatic crystals are deposited, containing a large quantity of water.

The salt fuses easily in its water of crystallization; as the heat is increased, the selenite sublimes unchanged. Sulphurous acid precipitates from the selenite a mixture of sulphate of mercury and selenium:

$$2\,(HgO,\,2\,SeO_2) + 9\,SO_2 =$$
$$Hg_2\,O,\,SO_3 + 8\,SO_3 + Se.$$

SELENITE OF LITHIA.

This salt is obtained by double decomposition. It is deliquescent. When heated, it fuses to a yellow liquid, and on cooling solidifies into an opaque crystalline mass, resembling mother-of-pearl. Selenite of lithia is soluble in selenious acid.

SELENITE OF YTTRIA.

Berzelius obtained the above as a white argillaceous precipitate, which was insoluble in selenious acid. When dry, it is a white amorphous powder, which at first gives off water when heated, and then acid.

SELENITES OF CERIUM.

Selenite of the protoxide of cerium is a white powder, insoluble in water. A biselenite of the same oxide is obtained by dissolving the former in selenious acid. Selenite of the sesquioxide of cerium is a citron-yellow powder, easily parting with its acid. The biselenite is obtained by dissolving the above in selenious acid. When evaporated on a water-bath, it leaves a yellow gummy mass, which, when heated, loses water, and becomes opaque and crystalline. It is soluble in water.

SELENITES OF ZIRCONIA.

The neutral salt is a white insoluble powder, obtained by double decomposition. It loses its acid when heated, and is soluble in selenious acid, yielding an acid salt.

SELENITES OF URANIUM.

Selenite of uranium is a citron-yellow powder that gives off acid when strongly heated, leaving a lower oxide; the bisalt yields, on evaporation, an opaque gum, behaving like the selenite of the sesquioxide of cerium. The formula for this salt is:

$$U_2\,O_3,\ 3\,SeO_2.$$

SELENITE OF TIN.

This salt is a white insoluble powder. It is soluble in hydrochloric acid, from which solution it is reprecipitated by water. Heated, it evolves first water, selenious acid then sublimes, and pure oxide of tin remains. The formula for the dry salt is:

$$SnO_2,\ 2\,SeO_2$$

I have now described the various compounds of this interesting acid. The difficulty of preparing the salts can only be known to the experimenter. Spontaneous evaporation, or double decomposition is the best way to obtain the desired end. Alcohol can seldom be employed as a precipitant, for it generally separates an oily liquid, which becomes crystalline only in rare instances. The determination of selenious acid is very difficult; fusion with nitrate of potash is the first step to convert the selenious into selenic acid, which latter can then be precipitated by nitrate of baryta; selenate of baryta must not be burned in the filter, as reduction readily takes place. To prevent loss, when the selenate of baryta is perfectly dry, it should be scraped from the filter into a weighed crucible, and the filter burned over it. The selenites seldom correspond with the sulphites or carbonates; where such is the case the analogy has been noticed. The great stability of selenious acid has been previously discussed. Its salts, when not deliquescent, are most persistent.

I shall close this memoir with a table of all the salts of selenious acid.

Selenite of potash . . .	. KO, SeO_2
Biselenite of potash . . .	. $KO, SeO_2 + HO, SeO_2$
Quadriselenite of potash . . .	. $KO, SeO +_2 3(HO, SeO_2)$?
Selenite of soda	. NaO, SeO_2
Biselenite of soda	. $NaO, SeO_2 + HO, SeO_2 + 2$ aq.
Quadriselenite of soda . . .	. $NaO, SeO_2 + 3(HO, SeO_2)$ + aq.
Selenite of ammonia . . .	. $NH_4 O, SeO_2$
Biselenite of ammonia . . .	. $NH_4 O, SeO_2 + HO, SeO_2$?
Selenite of baryta	. BaO, SeO_2
,, ,, strontia . . .	. SrO, SeO_2
,, ,, lime	. CaO, SeO_2
Biselenite of lime	. $CaO, SeO_2 + HO, SeO_2$?
Selenite of magnesia . . .	. $MgO, SeO_2 + 3$ aq.
,, ,, alumina	. $Al_2 O_3, 3 SeO_2 + 3$ aq.
Biselenite of alumina . . .	. $Al_2 O_3, 3 SeO_2 + 3 (HO, SeO_2)$?
Selenite of glucina	. $Gl_2 O_3, 3 SeO_2 + 3$ aq. ?
,, ,, chromium . . .	. $Cr_2 O_3, 3 SOe_2$
,, ,, iron	. FeO, SeO_2
Biselenite of iron	. $FeO, SeO_2 + HO, SeO_2$?
Selenite of the sesquioxide of iron	. $Fe_2 O_3, 3 SeO_2 + 4$ aq.
Sesquiselenite of the sesquioxide of iron	$2 Fe_2 O_3, 3 SeO_2$
Biselenite of the sesquioxide of iron	. $Fe_2 O_3, 3 SeO_2 + 3 (HO, SeO_2)$?
Selenite of manganese . . .	. $MnO, Se_2 O + 2$ aq.

Selenite of nickel	$NiO, SeO_2 + aq.$
,, ,, cobalt	$CoO, SeO_2 + aq.$?
,, ,, zinc	$ZnO, SeO_2 + 2 aq.$
,, ,, cadmium.	CdO, SeO_2
,, ,, copper	$3 (CuO, SeO_2) + aq.$
,, ,, the suboxide of copper	$Cu_2O, SeO_2 + aq.$?
,, ,, lead	PbO, SeO_2
,, ,, silver	AgO, SeO_2
,, ,, the suboxide of mercury	$Hg_2 O, SeO_2$
,, ,, the oxide of mercury	HgO, SeO_2
Biselenite of the oxide of mercury	$HgO, SeO_2 + HO, SeO_2$?
Selenite of lithia	LiO, SeO_2
,, ,, yttria	YO, SeO_2
,, ,, the oxide of cerium	CeO, SeO_2 ?
Biselenite of the oxide of cerium.	$CeO, SeO_2 + HO, SeO_2$?
Selenite of the sesquioxide of cerium.	$Ce_2 O_3, 3 SeO_2$?
Biselenite of the sesquioxide of cerium.	$Ce_2 O_3, 3 SeO_2 + 3 (HO, SeO_2)$?
Selenite of zirconia	$Zr_2 O_3, 3 SeO_2$
,, ,, uranium	$U_2 O_3, 3 SeO_2$
,, ,, tin	$SnO_2, 2 SeO_2$

All the preceding salts, heated on charcoal before the blow-pipe, impart a magnificent blue colour to the flame, emitting the unmistakeable and offensive smell of foul horse-radish. That many of them were obtained in definite crystals, is due in a measure to the extreme coldness of the weather. It is valuable, and interesting, to ascertain the composition of the salts of some of those acids, having *ous* for their termination. I purpose shortly communicating to the Society a paper on the Tellurites.

VI.—*On some newly discovered Substances from the African Guano Deposits.* *By* THORNTON J. HERAPATH, ESQ.

Some time in the latter part of the year 1845, a paper was read before this Society, by Mr. E. F. Teschemacher,* in which the author gives an account of the results of his analyses, including a variety of substances which had been found in the guano deposits and in their vicinity. Besides those there described, however, I have lately had the opportunity of examining another, which that gentleman does not appear to have taken any notice of. This substance, which was found occurring in large crystalline masses or nodules in a cargo of guano from the island of Ichaboe, on the western coast of Africa, was sent to my father's laboratory for examination, by Mr. Ruxton, of Swansea, in January, 1846, some of the parties to whom he had supplied the guano having complained to him of the presence of the crystals, imagining them to be an adulteration. These crystals, when purified from the adherent guano, were found to be perfectly transparent and homogeneous, but stained of a light yellowish-brown colour by the humic acid and extractive matters of the guano. They were exceedingly frangible, and did not effloresce upon exposure to the air; they dissolved easily both in hot and cold water, and the solutions gave, with the soluble salts of silver, a bright yellow precipitate, which was almost entirely soluble in an excess of nitric acid. When boiled with a solution of potassa, pungent fumes of ammonia were given off, which gave a fugitive stain to moistened turmeric paper. Before the blow-pipe, they intumesced, turned black, and gave off water and ammonia; by a further application of heat, the carbonaceous matters were burnt off, and the residue fused into a transparent colourless glass, which dissolved readily in boiling water, giving a solution which yielded a granular precipitate when tested with antimoniate of potash.

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* Mem. Chem. Soc. vol. III, part 16, p. 13.

The specific gravity of these crystals, as determined by means of oil of turpentine, was about 1·6151. An attempt was made to ascertain the primary form of the crystal, but it was found impossible to do so from the rough irregular masses met with in the guano. By dissolving these, however, in boiling water, and filtering the solution and crystallizing, the salt was obtained in moderately large, colourless, prismatic crystals. Upon subjecting these to analysis, the following results were obtained:

I. 10 grains of the salt, when heated to redness, lost 5·103 grs. of water and ammonia.

II. 10 grains, when treated as before, lost 5·243 grs. in weight.

III. 5 grains, when burnt with potash and lime by Varrentrapp and Will's process, gave 4·890 grs. of ammonio-chloride of platinum =0·377 grs. of ammonia.

IV. 5 grains, treated as before, gave 5·078 grs. of ammonio-chloride of platinum = 0·391 grs. of ammonia.

V. 10 grains, when dissolved in water, and the solution precipitated by neutral acetate of lead, gave 20·331 grs. of phosphate of lead, which, when decomposed by sulphuric acid, gave 22·938 grs. of sulphate of lead.

VI. 10 grains, treated as before, gave 19·549 grs. of phosphate, and 21·867 grs. of sulphate, of lead.

VII. 10 grains gave 3·002 grs. of chloride of sodium.

VIII. 10 grains gave 2·905 grs. of chloride of sodium.

These numbers give the following per-centage composition:

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	Mean.
$\overset{\cdot\cdot\cdot\cdot\cdot}{P}$	..	..	..	..	34·291	34·360	..	..	34·325
$\dot{Na}$			..	..	..	..	16·010	15·494	15·752
NH_3	51·030	52·320	7·540	7·820	..	..	..	..	7·680
$\dot{H}$			..	..	..	..	..	..	42·243

which very closely corresponds with that of the ammonio-phosphate of soda, or microcosmic salt, the formula for which is

$$\dot{Na},\ NH_3,\ \overset{\cdot\cdot\cdot\cdot\cdot}{Ph}+10\dot{H},$$

or according to Graham,

$$Na\,O,\ NH_4\,O,\ PO_5,\ HO+8HO.$$

The original crystals contained the following constituents in 100 parts as:

Crystallized ammonio-phosphate of soda	91·660
Organic matters, (urates, humates, &c.)	1·956
Phosphate of potash	evident traces.
Chloride of sodium	0·521
Carbonate of lime	0·280
Carbonate of magnesia	traces.
Phosphate of lime	2·100
Silica, sand, &c.	2·151
Water and loss	1·332
	100·000

With regard to the manner of the formation of this salt, it is extremely difficult to comprehend how such a compound as the ammonio-phosphate of soda could be produced by the decomposition of a substance so remarkably deficient in the alkalies as guano. For unless we can conceive that there was in this case a peculiar and special source of the soda, we must of necessity admit that it was obtained from the decomposition of the chloride of sodium of the sea-water by the phosphate of ammonia of the guano. The resulting chloride of ammonium being either volatilized at the high temperature of those climates, or, from its extreme solubility, dissolved out by the rain-water and carried into the sea or the lower strata of the guano deposits. We well know that chloride of sodium is capable of being decomposed by phosphate of ammonia at a high temperature. May not this decomposition, therefore, also take place when the salts are in solution ? I think it very probable.

This being the first instance in which the ammonio-phosphate of soda has been met with as a natural production, I propose to class it amongst our minerals under the name of "*Stercorite.*"* I should have preferred to have given it that of Guanite, as being more indicative of its origin, but this has been already applied by Mr. Teschemacher to the ammonio-magnesian phosphate, another product of the decomposition of guano.

I have also examined another salt which was met with in the same cargo of guano as the preceding, to which it bore a very close resemblance, both in physical and chemical properties. Like it, it was frangible, crystalline, and readily soluble in water, and gave off ammoniacal fumes when heated to redness or when treated with caustic potash; it also gave a yellow precipitate with nitrate of silver; but it differed from it in efflorescing upon exposure to the air, and in not giving a precipitate with antimoniate of potash.

The primary form of the crystal, as nearly as could be determined from the few imperfect specimens in my possession, was an oblique rhomboidal prism, with a dihedral summit. Upon redissolving these in water and recrystallizing by spontaneous evaporation, long acicular crystals were obtained, which, when dried between pieces of bibulous paper and subjected to analysis, afforded the following results :

I. 2·131 grains of the crystals, when heated to redness, lost 1·034 grs. in weight of water and ammonia.

II. 1·940 grains gave 6·039 grs. of ammonio-chloride of platinum =0·465 grs. of ammonia.

III. 3·500 grains gave 10·539 grs. of phosphate of lead, which gave 11·786 grs. of sulphate of lead=1·854 grs. of phosphoric acid.

Or, on 100 parts:

	I.	II.	III.	
Water . .	48·521	—	—	23·058
Ammonia .		23·980	—	23·980
Phosphoric acid	—	—	52·962	52·962

numbers which are very nearly equivalent to 1 atom of ammonia, 1 atom of phosphoric acid, and 1½ atoms of water. It may therefore be considered as the neutral *phosphate of ammonia*. The excess of water was doubtlessly caused by the moisture which remained between the interstices of the crystals. It was therefore the same salt as that which had been previously examined by Mr. Teschemacher, but which he was prevented from analyzing quantitatively on account of the smallness of the quantity in his possession.

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* From the Latin, "*Stercoro*," to dung or manure land.

In conclusion, I should perhaps observe that the guano from which the above substances were obtained was exceedingly moist, and possessed a very strong ammoniacal smell.

VII.—*Analysis of Thames Water.* *By* JOHN M. ASHLEY, ESQ.

When we reflect upon the almost countless uses to which the water of the River Thames is applied, it creates some surprise that no accurate analysis of its waters should have appeared until the commencement of last year.*

As no very certain knowledge of the composition of Thames water can be obtained by any other means than through the medium of a series of analyses of water taken at different places, it is the intention of Dr. Hofmann to have these analyses conducted in the laboratories of the Royal College of Chemistry, the present analysis forming the second investigation of the series.

The water analysed by Mr. Clark was obtained from Twickenham; that which I have used was taken from London Bridge, on the 13th of October, 1848, about half an hour after high water. It was a spring tide, and the water was unusually muddy. The hour of the day was three o'clock, P.M. The following data were observed:

Temperature of the water . . .	13° C = 55·4 F.
Temperature of the air	15° C = 59·0 F.
Specific gravity of the water	1·0001.

The qualitative analysis pointed out the presence of potash, soda, lime, magnesia, alumina, chlorine, sulphuric acid, silicic acid, and organic matter.

A very small amount of phosphoric acid was detected, but it was in too minute quantity for estimation.

After the evaporation of large amounts of water, neither bromine, iodine, nor manganese could be detected.

The following experimental numbers were obtained by quantitative determinations.

A. Determination of total amount of fixed constituents:

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* Mr. Clark on Thames water, Quarterly Journal of the Chemical Society, vol. i. p. 155.

Amount of water employed.	Amount obtained.	Per-centage.
I. 450·679 grm.	0·1859 grm.	0·041248
II. 564·5610 „	0·2283 „	0·040438
	Mean	0·040843

B. Determination of chlorine:

Amount of water employed.	Amount of chloride of sodium obtained.	Per-centage of chlorine.
I. 674·53 grm.	0·1737 grm.	0·006353
II. 419·66 „	0·1095 „	0·006478
	Mean	0·006394

C. Determination of sulphuric acid:

Amount of water employed.	Amount of sulphate of baryta obtained.	Per-centage of sulphuric acid.
I. 609·96 grm.	0·0512 grm.	0·002883
II. 703·181 „	0·0502 „	0·002452
	Mean	0·002667

D. Determination of silicic acid:

Amount of water employed.	Amount of silicic acid obtained.	Per-centage of silicic acid.
I. 1280·9110 grm.	0·0227 grm.	0·000177
II. 1300·1560 „	0·0232 „	0·000178
	Mean	0·000177

E. Determination of lime and magnesia:

Amount of water employed.	Amount of carbonate of lime obtained.	Per-centage of lime.
a. I. 1280·9110 grm.	0·2651 grm.	0·011589
II. 1300·1560 „	0·2657 „	0·011444
	Mean	0·011516

b. Determination of magnesia in filtrate from oxalate of lime:

Amount of water employed.	Amount of pyro-phosphate of magnesia obtained.	Per-centage of magnesia.
I. 1280·9110 grm.	0·0527 grm.	0·000142
II. 1300·1560 „	0·0494 „	0·000140
	Mean	0·000140

F. Determination of alkalies:

Amount of water employed.	Amount of mixed chlorides obtained.
I. 2099·889 grm.	0·3074
II. 2071·420 „	0·2936

a. Determination of potash:

Amount of water employed.	Per-centage of platinum and potassium obtained.	Per-centage of potash.
I. 2099·889 grm.	0·2494 grm.	0·000228
II. 2071·4200 „	0·2040 „	0·000189
		Mean 0·000208

b. Determination of soda.

Amount of water employed.	Amount of chloride of sodium obtained.	Per-centage of soda.
I. 2099·889 grm.	0·2313 grm.	0·005881
II. 2071·4200 „	0·2304 „	0·005918
		Mean ·005899.

15309 grms. of the water were evaporated down to 801·47 grms. The precipitate which formed was separated, and weighed 3·1115 grms.

Determination of organic matter in the filtrate:

Amount of filtrate employed.	Amount of organic matter burnt off.	Per-centage upon the whole amount of water.
I. 132·980 grm.	0·0956 grm.	0·003763
II. 136·2000 „	0·0759 „	0·002917
		Mean 0·006656

Determination of organic matter in the precipitate:

Amount of precipitate employed.	Amount of organic water burnt off.	Per-centage upon the whole amount of water.
I. 1·9350 grm.	0·6407 grm.	0·006734
II. 0·4610 „	0·1471 „	0·006479
		0·003340

Determination of carbonic acid:

At the time of collecting the water, a syphon capable of containing 534 cubic centimetres of distilled water was filled twelve times, and discharged into four bottles containing chloride of calcium and ammonia. The precipitate which had formed in all the bottles weighed 3·6067 grms.

Amount of precipitate employed.	Amount of carbonic acid evolved.	Amount calculated on the whole precipitate.
I. 0·4226 grm.	0·1200 grm.	0·535662
II. 0·5144 „	0·1560 „	0·521738
		Mean 0·528700

Per-centage in the water 0·016495

From the analytical results, the following composition of the water is deduced :

	In 100 litres. (Grammes.)	In a gallon. (Grains.)
Sulphate of potash	·385	·2695
Sulphate of soda	4·436	3·1052
Chloride of sodium	3·389	2·3723
Chloride of magnesium	·114	·0798
Chloride of calcium*	9·963	6·9741
Chloride of lime	11·595	8·1165
Silicic acid	·177	·1239
Phosphoric acid	traces	traces
Alumina	traces	traces
Insoluble organic matter	6.656	4·6592
Soluble organic matter	3·340	2·3380
	40·055	28·0385
Direct determination of fixed constituents	40·843	28·5901

Having deducted from the total amount of carbonic acid, the amount required to combine with the lime, the amount of free carbonic acid is 0·005105 grm., corresponding to 27·1906 cubic centimetres in a litre, or to 8·8076 cubic inches in an imperial gallon. The greatest difference between Mr. Clark's analysis and my own, consists in the variation in the amounts of soluble salts; the soluble salts found by Mr. Clark amount to only 6·3118, while I obtain as much as 18·287. A proportionate difference exists in the relative amounts of organic matter.

My best thanks are due to Professor Hofmann for the many attentions and kindness that I have received from him during the above investigation.

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* On the principle of combining the strongest bases with the strongest acids, in this analysis as well as in that of Mr. Clark, chloride of calcium is enumerated along with sulphate of soda, although we may assume, that the constituents of these two salts are actually in solution in the form of sulphate of lime and chloride of sodium.

February 5, 1849.

Thos. Graham, Esq., Vice-President, in the Chair.

A specimen of a phosphatic earth from the green sand formation of the south of England, was presented by Mr. J. T. Herapath to the Society's Museum.

This substance is now often substituted for bone-earth in the preparation of superphosphate of lime for agricultural purposes.

It contains, according to Mr. Herapath's analysis:

Organic matter	traces.
Silica, with some silicate of alumina and silicate of iron	13·240
Alkaline salt	traces.
Carbonate of lime	28·400
,, magnesia	traces.
Sulphate of lime	0·736
Phosphate of lime (tribasic)	21·880
" magnesia	traces.
Perphosphate of iron	24·760
Phosphate of alumina	7·032
Fluoride of calcium	traces.
Water	3·400
Lost	0·552
	100·000

The following paper was read:

VIII.—*Analyses of the mineral constituents of the Flax plant, and of the soils on which the plants had been grown.*

By J. E. MAYER *and* J. S. BRAZIER, ESQRS.

The daily increasing extent to which flax is cultivated by the farmer, necessarily directed the attention of chemists to the analysis of this plant, soon after the importance of the mineral constituents, strangely neglected for a considerable period, had been generally acknowledged by the scientific agriculturist.

We owe to Sir Robert Kane two excellent papers, containing the analyses both of the ashes of different specimens of flax, and of the soils on which they had been cultivated.* These specimens had been grown principally in Belgium and Holland, where the greatest care is taken in preparing and manuring the land. The analyses which we intend to communicate in the following pages, were made with different specimens of Russian growth. They were supplied to us by Dr. Hofmann,* under whose guidance we have worked throughout.

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* Philosophical Magazine, vol. XXXI. p. 43.

The localities from which we have obtained our specimens of Flax, are the Russian districts known as Esthonia, or Estland, Livonia or Lievland, Courland, and Lithuania. The first of these districts, with the second and third mentioned, are situated on the eastern shores of the Baltic; the fourth, Lithuania, is the only inland country.

These countries extend from 48^0 to 60^0 north latitude, and from 22^0 to 28^0 east longitude.

The plan we adopted for the preparation of the ash, was the following :—A handful of stems, after being inflamed, were held over a porcelain dish, and allowed to burn gently. The ashes collected in the dish by this process, in one or two instances, were remarkably white; however, in order to free them still more from the remaining carbon, they were placed, small quantities at a time, in a platinum dish over a gentle gas flame. In this manner also the sulphides, formed in the process of combustion, were entirely reconverted into sulphates. This conversion was proved by experiment previous to analysis. In order to hasten the latter part of the process, the Lithuanian and Estland ashes were burned with protoxide of mercury.

The general analyses were performed in the usual manner :—the experimental numbers in Table I. shew the quantities of substance employed, the results from which are exhibited in Table II.

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* I am indebted for these specimens to the kindness of Mr. Arthur Marshall, of Leeds, who had them sent from Russia for analysis, being originally intended to supply the material for a continuation of Sir Robert Kane's researches; and it was only in consequence of Sir Robert's other avocations preventing him from following up the investigation any further, that Mr. Marshall sent them to the Laboratory of the Royal College of Chemistry.—Dr. A. W. Hofmann.

TABLE I.

	Lievland.		Courland.		Lithuanian.		Estland.	
	I.	II.	I.	II.	I.	II.	I.	II.
	grm.	grm.	grm.	grm.	grm.	grm.	grm.	grm.
Quantity of ash employed for the general analysis . . .	4·7076	4·6640	5·3100	1·2953	6·1526	5·8256	4·4630	
Whole amount of the hydrochloric acid solution	324·0300	197·5950	293·495	293·495	242·5620	206·9200	280·7400	
Hydrochloric acid solution employed for the alkalies . .	17·5040	16·8415	24·2960	27·4094	28·8473	28·1370	20·3340	23·9870
Hydrochloric acid solution employed for sulphuric and phosphoric acids	27·8896 29·1392	30·7767	26·6230	27·1031 27·2480	27·4080	28·0232	22·7710 22·6950	23·0280
Hydrochloric acid solution for sesquioxide of iron, lime and magnesia	30·2702	30·7767	31·7940 19·9430 31·7940	21·9975 19·2260 27·5790	28·8495 28·4630	25·4352	28·0500 22·7700	25·8150 19·7130
Quantity of ash employed for the estimation of chlorine . .	2·0813	1·3249	·8360	....	1·0017	....	1·3159	....
Quantity of ash employed for the estimation of carbonic acid .	·8532	·8875	·7023	·8097	·8017	·7480	·9680	·8418
Quantity of the plant dried at 100° C. for the estimation of the amount of ash	6·0140	5·4247	1·4577	....	3·3575	....	2·4930	....

TABLE II.

	Lievland.		Courland.		Lithuanian.		Estland.	
	I.	II.	I.	II.	I.	II.	I.	II.
	grm.	grm.	grm.	grm.	grm.	grm.	grm.	grm.
Silicic acid	0·3098	0.3260	0.3590	0·0868	0.2850	0·2597	0.2010	.. ..
Sand and charcoal	0·3240	0.0128	0.1485	0·0331	0.0750	0·0689	0.1145	.. ..
Mixed chlorides of potassium and sodium	2·6678	2.6492	2.8690	2·8736	3.1279	3·1203	2.3332	2·3349
Bichloride of platinum and potassium	8·7439	8.6829	8.1660	8·1734	8.8082	8·7819	5.3430	5·3521
Chloride of sodium	.. ..	.. ..	0.3778	0·3797	0.4407	0·4409	0.7030	0·7001
Sulphate of baryta for sulphuric acid	0·6369	0.6382	0.7222	0·6692	0.4299	0·5047	0.5424	.. ..
Pyrophosphate of magnesia for phosphoric acid	0·6492	0.6504	0.5512	0·5601	1.0257	1·0394	0.9710	0.9813
Phosphate of sesquioxide of iron	0·1338	0.1333	0.1477	0·1413	0.1513	0·1459	0.1252	0.1301
Carbonate of lime	1·4451	1.4314	1.8998	1·9077	1.9832	1·9955	1.8913	1.8814
Pyrophosphate of magnesia for magnesia	0·8028	0.7324	0.9046	0·8801	0.8818	0·9592	1.3006	1.2817
Chloride of silver	0·0409	0.0277	0.0320	.. ..	0.0692	.. ..	0.0487	.. ..
Carbonic acid	0·1500	0.1550	0.1300	0·1500	0.1830	0·1700	0.0750	0·0650
Amount of ash left on incineration	0.2532	0.2240	0.0530	.. ..	0.0773	.. ..	0.1020	.. ..

These numbers correspond to the following composition per cent.

I.—LIEVLAND FLAX ASH.

The stems, upon incineration, gave in average 4·1292 per cent of ash.
Composition of the ash directly found:

	I.	II.	MEAN.
Potash . . .	35·0670	34·8588	34·9629
Lime . . .	17·1892	17·1833	17·1862
Magnesia . .	6·2197	6·3278	6·2738
Sesquioxide of iron.	0·9235	0·9286	0·9260
Chloride of potassium	1·0849	1·0201	1·0525
Phosphoric acid .	8·8048	8·8224	8·8136
Sulphuric acid .	4·5097	4·6012	4·5554
Silicic acid . .	6·5812	6·9216	6·7514
Carbonic acid .	17·5914	17·4648	17·5281
Sand and charcoal .	0·6788	0·3425	0·5106
	98·6502	98·4711	98·5605

The above numbers, after deducting sand and charcoal, which are considered but as accidentally present, and also carbonic acid, give the following composition per cent:

Potash	43·42
Lime.	21·35
Magnesia	7·79
Sesquioxide of iron . .	1·15
Chloride of potassium . .	1·31
Phosphoric acid . . .	10·94
Sulphuric acid . . .	5·66
Silicic acid . . .	8·38
	100·00

II.—COURLAND FLAX ASH.

The stems, upon incineration, gave in average 3·6358 per cent of ash.
Composition of the ash directly found:

	I.	II.	MEAN.
Potash . . .	29·6786	29·5988	29·6387
Soda	2·9640	2·9433	2·9536
Lime	20·1184	20·0355	20·0769
Magnesia . . .	6·1111	6·2123	6·1617
Sesquioxide of iron .	0·9038	0·8646	0·8842
Manganese . . .	trace	trace	trace
Chloride of sodium .	1·5562	1·5562	1·5562
Phosphoric acid . .	6·5948	6·7027	6·6487
Sulphuric acid . .	4·6647	4·3220	4·4933
Silicic acid . . .	6·7027	6·7604	6·7316
Carbonic acid . .	18·5106	18·5253	18·5179
Sand and charcoal. .	2·5559	2·7966	2·6762
	100·3608	100·3177	100·3390

Per-centage after deducting sand, charcoal and carbonic acid:

Potash	37·44
Soda	3·74
Lime	25·39
Magnesia	7·71
Sesquioxide of iron	1·13
Chloride of sodium	1·94
Phosphoric acid	8·31
Sulphuric acid	5·89
Silicic acid	8·45
	100·00

III.—LITHUANIAN FLAX ASH.

The stems, upon incineration, gave in average 2·3023 per cent of ash.

Composition of the ash directly found:

	I.	II.	MEAN.
Potash	27·5459	27·4770	27·5114
Soda	2·3055	2·3065	2·3060
Lime	18·0526	18·1648	18·1087
Magnesia	5·6794	5·5154	5·5974
Sesquioxide of iron	0·7991	0·7710	0·7850
Chloride of sodium	2·8115	2·8115	2·8115
Phosphoric acid	10·5868	10·8972	10·7420
Sulphuric acid	2·6755	2·8137	2·7446
Silicic acid	4·6346	4·4532	4·5439
Carbonic acid	22·8302	22·7272	22·7787
Sand and charcoal	1·2190	1·1828	1·2009
	99·1401	99·1203	99·1301

Per-centage after deducting sand, charcoal and carbonic acid:

Potash	36·61
Soda	3·06
Lime	24·09
Magnesia	7·45
Sesquioxide of iron	1·04
Chloride of sodium	3·75
Phosphoric acid	14·30
Sulphuric acid	3·65
Silicic acid	6·05
	100·00

IV.—ESTLAND FLAX ASH.

The stems, upon incineration, gave in average 4·0914 per cent of ash. Composition of the ash directly found:

	I.	II.	MEAN.
Potash	23·1083	23·0432	23·0757
Soda	7·5111	7·5323	7·5217
Lime	23·8567	23·6070	23·7318
Magnesia	10·6274	10·4718	10·5496
Sesquioxide of iron	0·9115	0·9363	0·9239
Chloride of sodium	1·5069	1·5069	1.5069
Phosphoric acid	13·8098	13·9642	13·8870
Sulphuric acid	4·1678	4·1678	4·1678
Silicic acid	4·4815	4·4815	4·4815
Carbonic acid	7·7559	7·7215	7·7387
Sand and charcoal	2·5878	2·5878	2·5878
	100·3247	100·0203	100·1724

Per-centage after deducting sand, charcoal and carbonic acid:

Potash	25·70
Soda	8·37
Lime	26·41
Magnesia	11·74
Sesquioxide of iron	1·02
Chloride of sodium	1·67
Phosphoric acid	15·47
Sulphuric acid	4·64
Silicic acid	4·98
	100·00

From the foregoing analyses, the following comparative table has been made, from which it will be readily seen, in what points the ashes of these different specimens agree in composition.

	Lievland. I.	Courland. II.	Lithuanian. III.	Estland. IV.
Potash	43·42	37·44	36·61	25·70
Soda	—	3·74	3·06	8·37
Lime	21·35	25·39	24.09	26·41
Magnesia	7·79	7·71	7·45	11·74
Sesquioxide of iron	1·15	1·13	1·04	1·02
Manganese	—	trace.	—	—
Chloride of sodium	—	1·94	3·75	1·67
„ „ potassium	1·31	—	—	—
Phosphoric acid	10·94	8·31	14·30	15·47
Sulphuric acid.	5·66	5·89	3·65	4·64
Silicic acid	8·38	8·45	6·05	4·98
	100·00	100·00	100·00	100·00

We also append, in a tabular form, the results of Sir R. Kane's analyses of this plant, taken from his paper, read before the Royal Dublin Society, on the 6th of April, 1847.

To facilitate comparison, we have re-calculated these analyses after deducting the carbonic acid.

	A	B	C	D	E	F	G
	Courtrai District.		Antwerp District.				
	Heestelt.	Escamaffles.	Hammezog.	Not named.	District in Holland.	Dublin.	Armagh.
Potash . . .	9·69	30·62	26·67	28·62	21·35	11·78	6·60
Soda . . .	24·16	none.	16·88	0·48	12·65	11·82	6·61
Lime . . .	19.37	22·04	22·15	21·19	21·30	14·85	23·67
Magnesia . . .	4·34	4·45	4·70	4·05	3·50	9·38	4·22
Sesquioxide of iron . .	5·66	2·03	1·31	2·53	2·74	,, ,,	14·10
Alumina . . .	0·56	0·58	0·86	,, ,,	1·67	7·32	,, ,,
Manganese . . .	trace.	trace.	trace.	,, ,,	,, ,,	,, ,,	1·12
Sulphuric acid . .	7·93	8·33	8·18	13·43	11·22	3·19	9·30
Phosphoric acid . .	14·10	15·78	10·66	12·19	12·82	13·05	7·29
Silicic acid . . .	3·85	4·54	3·20	3·36	6·18	25·71	0·94
Chloride of sodium . .	10·34	11·63	5 49	14·15	6 57	2 90	26 15
	100·00	100·00	100·00	100 00	100 00	100·00	100·00

On comparing the results of our analyses with those of Sir Robert Kane, we find at once that the general features of both are identical, although, as might be expected, discrepancies present themselves respecting the individual constituents. In the ashes, both of the Belgian and of the Russian specimens, we meet with a very large amount of alkali (nearly 40 per cent): the quantity, too, of phosphoric acid is very considerable (from 10 to 15 per cent). Our analyses then furnish a further proof that flax must be classed among the most exhausting crops, for, the amount of valuable mineral substances which we remove from the soil in this plant considerably exceeds the quantity which is generally extracted from it in the form of wheat or corn.

From a statement of Mr. Mac Adam,* it appears that one rood of land yields about 12·7 cwt. of recently-pulled flax plant. If we take this number as the basis of calculation, and the average percentage of ash, at 3·53 lbs., of alkalies, at 39·58 lbs., and of phosphoric acid, at 12·51 lbs., we find that a flax crop removes from a rood of land not less than 12·21 lbs. of alkalies, and 5·94 lbs. of phosphoric acid; on the other hand, we have learnt from the researches of Mr. Way,* that a rood of land, which has served for the cultivation of wheat, loses (an average taken from a great number of analyses) about 7·5 lbs. of alkali and 6·9 lbs. of phosphoric acid. These figures show that the amount of phosphoric acid in the flax crop closely approaches that of the wheat, whilst the latter extracts only about half the quantity of alkali which we find in the former. Hence, it would appear, that a flax crop is at least as exhausting as a crop of wheat.

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* Royal Agricultural Journal, vol. VIII, p. 361.

There is, however, one striking point of dissimilarity between the cultivation of wheat and that of flax, and we are indebted to Sir Robert Kane for having for the first time brought this point under the notice of the farmer in a forcible manner—viz: that while the mineral ingredients which we remove from our fields in wheat, or cerialiæ in general, become constituents of food, and enter in this manner into a circulation, from which, even under very favourable circumstances, they return to the soil only after the lapse of some time; the woody fibre of flax, as a necessary preliminary to its being used by man, is separated to a considerable extent from those very mineral substances, which are so essential for its successful growth. This mineral matter, when economized in a proper manner by the farmer, may be returned to his field to keep up the equilibrium of its fertility.

The vegetation of the flax plant resembles in this respect the growth of the sugar-cane, from the culture of which, we expect a material consisting entirely of atmospheric constituents. The inorganic substances taken up by the plant are only instruments used in its production, which should be as carefully preserved as tools in a manufactory, and will then do further duty in promoting the elaboration of future crops.

The analysis of the flax ash suggests a few remarks respecting an interesting feature in the nature of ashes generally, which was first noticed by Professor Liebig in his celebrated Agricultural Chemistry. On comparing the composition of the ashes of specimens of the same plant, cultivated under different circumstances, he observed, that notwithstanding very considerable discrepancies in the constitution, the entire basic power of the different bases united with a certain class of acids, for instance, the organic acids, remained constant for different specimens of the same plant: or in other words, the basicity of an oxide being measured by its oxygen, the total amount of oxygen contained in the bases forming organic salts, was found to be identical in the different specimens. The views respecting this typical basicity, which Liebig pointed out in a few instances, and only for the salts of organic acids, were afterwards extended by other chemists. Indeed, the total amount of oxygen contained in the form of basic oxides seems to vary only within narrow limits for different individuals of the same class of plants. Sir Robert Kane has calculated the quantity of oxygen in the bases of his flax ashes, the constancy of which certainly seems to support this view; our analyses lead to a similar conclusion, as may be seen from the following figures:

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* Royal Agricultural Journal, vol. VII. p. 593.

Name of the ash.	Quantity of basic oxygen in 100 parts.	Name of the ash.	Quantity of basic oxygen in 100 parts.
Heestert . . .	16·95	Lievland	16·80
Escamaffles . . .	14·00	Courland	17·89
Hamme Zog . .	17·71	Lithuanian	17·12
Unknown district .	13·36	Estland	17·86
Holland . . .	15·83		
Dublin	16·36		*Mean* 17·42
Armagh	15·68		
	Mean 15·68		

The composition of several wheat-ashes, as resulting from Mr. Way's analysis, likewise appears to be favourable to this view.*

Specimen	No. 1.	Hopeton wheat	11·64	per cent.
,,	No. 2.	Creeping wheat	11·52	,,
,,	No. 3.	Red straw white wheat . .	11·02	,,
,,	No. 4.	Hopeton wheat, No. 2 . .	11·94	,,
,,	No. 5.	French wheat	12·59	,,
,,	No. 6.	Egyptian wheat.	12·19	,,
,,	No. 7.	Odessa wheat	12·08	,,
,,	No. 8.	Marianople wheat	14·46	,,
,,	No. 9.	Hopeton wheat, No. 3 . .	12·89	,,
,,	No. 10.	Red straw white wheat. .	11·53	,,
,,	No. 11.	White wheat	12·24	,,
		Mean	12·19	

The argument, however, drawn from these ashes, is of minor importance, the discrepancies in their composition being far less conspicuous than in the former cases.

The number representing the basic power of the sum of the metallic oxides in the ash varying within trifling limits, it is but a natural consequence that we should likewise find a certain constancy in the acidity of the total amount of acids. Without going into detail, a glance at the tables will shew, indeed, that a replacement of the acids occurs to a certain extent. Whenever the amount of carbonic acid, which represents the organic acids, diminishes, we find the quantity of inorganic acid, as sulphuric and phosphoric, increases, and *vice versâ*.

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* Royal Agricutural Society Journal, vol. vii. p. 666.

Our attention was next directed to the soils upon which the different specimens of flax had been grown, samples of which, through the kindness of Mr. Marshall, had likewise been forwarded to Dr. Hofmann.

These soils all gave a brownish colour to boiling water, owing to a portion of the organic matter being soluble in that menstruum.

The following table shews the behaviour of these soils with solvents:

		Lievland.	Courland.	Lithuania.	Estland.
Soluble in water.	Inorganic matter .	0·0864	0·1700	0·1528	0·1497
	Organic matter . .	0·2290	0·3125	0·4417	0·4578
	Total	0·3154	0·4825	0·5945	0·6075
Soluble in hydrochloric acid		7·2596	6·9166	7·2433	8·7119
Insoluble residue		92·4250	92·6009	92·1622	90·6806
		100·0000	100·0000	100·0000	100·0000

The following tables contain the details of the individual determinations:—

TABLE I.

	Lievland.	Courland.	Lithuanian.	Estland.
	grm.	grm.	grm.	grm.
Quantity of soil employed for general analysis . . .	20·0480	22·3010	18·5560	22·9480
Amount of the hydrochloric solution	270·0400	232·3550	324·1250	263·98
Hydrochloric solution for alkalies	64·1800	67·4600	74·3800	56·1600
Hydrochloric solution for sulphuric acid	58·0350	65·2700	69·9400	45·53
Hydrochloric solution for phosphoric acid, sesquioxide of iron, alumina, lime and magnesia	84·3700 73·4400	69·7700	75·9150	88·7600 50·9400
Hydrochloric solution for the sesquioxide of iron	23·8400	46·9195	60·7950	22·1800
Quantity of soil for chlorine .	13·2600	11·3701	11·6611	14·4190
Quantity of soil for total amount of organic matter	7·5850	4·9130	5·6485	7·3205
Quantity of soil for total amount soluble in water . . .	164·8400	205·1700	228·2350	104·6100

TABLE II.

	Lievland.	Courland.	Lithuan.	Estland.
Residue	18·5294	20·7465	17·1003	20·8094
Mixed chlorides of potassium and sodium .	0·1684	0·1757	0·1839	0·1738
Bichloride of platinum and potassium. .	0·5217	0·3758	0·5255	0·4419
Chloride of sodium	0·0091	0·0609	0·0236	0·0388
Sulphate of baryta for sulphuric acid . .	0·0999	0·0543	0·0784	0·8897
Pyrophosphate of magnesia for phosph. acid	0·0448	0·0190	0·0234	0·0577
Sesquioxide of iron and alumina . .	0·6214	0·9477	0·9864	0·9250
Sesquioxide of iron	0·3624	0·5300	0·5911	0·4537
Carbonate of lime	0·1504	0·3113	0·1494	0·3237
Pyrophosphate of magnesia for magnesia .	0·1103	0·1075	0·0918	0·2228
Chloride of silver for chlorine . . .	0·0150	0·0071	0·0123	0·0280
Amount of soil left after ignition . .	7·2120	4·7150	5·4031	6·9645

From the former tables we obtain, by calculation, the following amounts of constituents of 100 parts in the soils:—

	Lievland.	Courland.	Lithuan.	Estland.
Potash	0·5011	0·3241	0·5466	0·3726
Soda	.. ..	0·1320	0 0452	0 0480
Lime	0·3751	0·7816	0·4980	0·7955
Magnesia	0·2006	0·1304	0·1805	0·3619
Alumina	1·1919	1·8731	2·1418	2·0102
Sesquioxide of iron . . .	1·8076	2·3767	3·1900	2·0206
Manganese	trace.	trace.	trace.	trace.
Chloride of sodium . . .	0·0455	0·0247	0·0421	0·0790
Sulphuric acid	0·1539	0·0880	0·1206	0·1618
Phosphoric acid	0·1399	0·0538	0·0805	0·1597
Organic matter	4·7176	4·0300	4·3442	4·8630
Insoluble residue after deducting organic matter . .	91·0634	89·4872	88·4724	88·2364
	100·1966	99·3016	99·6619	99·1087

The insoluble residue constituting the greater portion of the soil, was fused with carbonate of potash. The following are the experimental numbers:—

	Lievland.	Courland.	Lithuania.	Estland.
Amount of residue employed	0·9790	1·2955	0·8620	0·9780
Amount of hydrochloric acid solution obtained	82·35	213·9450	270·3300	91·9300
Amount of hydrochloric solution for the determination of sesquioxide of iron and alumina	17·11	26·9730	29·5835	30·1800
Amount of hydrochloric solution for the determination of lime	..	27·7520	26 0968	26·1700

	Lievland.	Courland	Lithuania.	Estland.
Amount of silicic acid obtained . .	0 852	1.1353	0·7958	0·8930
Amount of sesquioxide of iron and alumina obtained	0·0260	0·0106	0·0023	0·0210
Amount of carbonate of lime obtained .	..	0·0061	0·0015	0·0120

The insoluble residues, upon calculation, yield the following results per cent.

	Lievland.	Courland.	Lithuania.	Estland.
Lime	traces.	1·8727	0·8778	2·0120
Alumina	11·6270	6·1145	2·2452	5·7549
Sesquioxide of iron . .	traces.	traces.	traces.	traces.
Phosphoric acid . .	traces.	traces.	none.	traces
Silicic acid . . .	79·3424	81·5000	85·0938	80·5676
	90·9694	92·6224	88·2168	88·3345

In all the four soils we find, comparatively speaking, considerable quantities of alkali, especially potash, and also of phosphoric acid. They closely resemble the Belgian soils analysed by Sir Robert Kane, as may be seen from the tables, which we borrow from Sir Robert's paper.

	Heestert.	Escamaffles.	Hamme Zog.	Not named.	Holland.
Potassa	0·160	0·123	0·068	0·151	0·583
Soda	0·298	0·146	0·110	0·206	0·306
Lime	0·357	0·227	0·481	0·366	3·043
Magnesia	0·202	0·153	0·140	0·142	0·105
Alumina	2·102	1·383	0·125	0·988	5·626
Sesquioxide of iron . . .	3·298	1·663	1·202	1·543	6·047
Manganese	trace	trace	a trace	no trace	trace
Chloride of sodium . . .	0·017	0·030	0·067	0·009	0·023
Sulphuric acid	0·025	0·017	0·013	0·026	0·023
Phosphoric acid	0·121	0·152	0·064	0·193	0·159
Organic matter not driven off at 100⁰ per cent .	3·123	2·361	4·209	3·672	5·841
Clay	14·920	9·280	5·760	4·400	17·080
Sand	75·080	84·065	86·797	88·385	60·947
	99·703	99·600	99·975	100·081	99·783

In conclusion, we beg to express our warmest thanks to Dr. Hofmann for his instruction and valuable advice during the prosecution of these analyses, and for the uniform kindness we have at all times experienced at his hands.

NOTICES

OF

PAPERS CONTAINED IN THE FOREIGN JOURNALS.

On a modification of phosphorus.—The red colour which phosphorus is observed to assume when exposed to the light, has been ascribed by Berzelius to an allotropic condition of the elements, while other chemists, amongst whom is Gmelin, have thought it probable that the phosphorus which is thus subject to redden, even in the presence of inert gases or in vacuo, cannot have been perfectly dry, and acquires its red colour by contamination with the red oxide of phosphorous, produced by the decomposition of the water, from which the colourless phosphorus has not been thoroughly separated. M. Schroetter dried colourless phosphorus at a temperature of 212° F. in an atmosphere of carbonic acid gas, and exposed it, surrounded by the same gas, in a vessel hermetically sealed, to the action of direct and indirect light; in both cases the phosphorus was reddened, and the rapidity with which this colouring ensued, was in proportion to the intensity of the light. These experiments prove that oxidation is not the cause of the phenomenon. The effects produced by light upon phosphorus, may likewise be obtained by a high temperature. M. Schroetter heated dry phosphorus in an apparatus entirely void of oxygen. The element distilled at a temperatue of 302° F. and condensed again in colourless drops; when, however, the temperature was raised to 439° F., the heated mass assumed a carmine-red colour, which became gradually deeper, and at length the whole was rendered perfectly opaque. This change in the character of the phosphorus is not sudden; on the increase of temperature a red powder is first observed, which, from its greater weight, falls to the bottom of the vessel containing the fused mass, and if the operation be kept up for 50 or 60 hours at a temperature ranging between 464° and 482° F., the greater portion of the lower part of the vessel becomes filled with this red substance, while the upper layers of the liquid are coloured more or less intensely from admixture with it. The conversion of phosphorus into this red modification is not effected under a pressure inferior to 393 millimeters (15,4842 in.), the boiling point being then below 439° F., which is the lowest limit of temperature compatible with its production. That the red body in question is simply phosphorus in an allotropic condition has been proved by the isolation of the substance, and its reconversion into ordinary phosphorus, at a temperature somewhat higher than that at which it was formed. The red substance may be isolated by a careful process of distillation, or by treating the mixture of the two modifications with bisulphuret of carbon, in which the red amorphous powder is insoluble, while the ordinary phosphorus is dissolved with ease. Thus separated, amorphous phosphorus may be purified by successively boiling with a solution of potash, water, water acidulated with nitric acid, and, lastly, with pure water. It then presents a more or less dark-red or even brown colour, and is totally without crystalline structure. Its density at 50° F. is 1·964; that of liquid phosphorus, at 113° F., being 1·88, and that of solid phosphorus, according to the author's own experiments, 1·83 at 50° F.

Amorphous phosphorus may be exposed to air without change, it is insoluble in alcohol, ether, naptha and protochloride of phosphorus; oil of turpentine, and, in general, all the liquids that boil at elevated temperatures, dissolve small quanties of it at the boiling point; but no substance that dissolves this body at a high temperature deposits it in the amorphous state on cooling. Heated in a tube filled with an atmosphere of carbonic acid in an oil-bath, amorphous phosphorus begins to change into the ordinary modificatiou at a temperature of 500° F. If the air has access to the phosphorus at this temperature, it inflames, but in order to convert the whole of it into phosphoric acid, the temperature must be raised to 572° F. This modification of phosphorus emits no luminous appearance in the dark, unless heated to nearly that point at which it inflames.

Amorphous phosphorus exerts much less affinity for the other elements than the common modification, and is insoluble like the latter; when it does enter into combination, the light evolved is very much less intense than is the case with white phosphorus; it is, however, capable of removing oxygen from a large number of metallic oxides, aided either by friction or heat, and the reaction is accompanied by the production of light.

*On a new mode of employing sulphuretted hydrogen in chemical analysis.**— Sulphuretted hydrogen has not been generally employed in chemical analysis, otherwise than as a reagent in the moist way. M. Ebelmen proposes to employ the gas as a means of converting mixtures of several bodies into sulphurets in the dry way, which sulphurets may then be separated from each other, either by the solubility of the one in acid, to the exclusion of the other, or the one may remain fixed, while the other is volatile at a slightly elevated temperature.

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* Ann. de Chim. et de Phys., xxv. 92.

The separation of *manganese* from *cobalt* may be very accurately effected in the following manner: The weighed mixture of the two oxides is placed in a small platinum dish, and heated to dull redness in a tube through which a current of sulphuretted hydrogen gas is passing. The mixed sulphurets, after being cooled in a current of the gas, are then removed and treated with cold water acidulated with hydrochloric acid. The sulphuret of manganese is alone dissolved. After a digestion of some hours, the liquid is filtered, and from the filtrate after boiling, the manganese can be precipitated by potash. The black residue of sulphuret of cobalt is decomposed by nitric acid, and the oxide of cobalt likewise precipitated by caustic potash.

Manganese may be separated from *nickel* with equal accuracy by this process.

Manganese cannot be accurately separated from *zinc* upon this plan, a small quantity of manganese remaining with the sulphuret of zinc when the mixed sulphurets are treated with acetic acid; hydrochloric acid is not applicable as the solvent of the manganese, as it likewise dissolves the sulphuret of zinc.

A mixture of the sulphurets of *iron* and *cobalt* obtained in this manner cannot be separated by hydrochloric acid, even when concentrated acid is employed: nearly the whole of the sulphuret of iron being retained by the sulphuret of cobalt. The insolubility of the sulphuret of iron insoluble in cold hydrochloric acid, does not, however, admit of its being thus separated from sulphuret of manganese, as a considerable proportion of the manganese is found to be irremoveable from the sulphuret of iron by the acid.

The volatility of certain of the sulphurets can sometimes be applied as a means of separating them quantitatively from others which are not volatile. Two instances are stated by M. Ebelmen; the one with reference to the separation of *iron* from *arsenic*, the other with reference to that of *arsenic* from *tin*.

Arseniate of iron is completely converted by heat in a current of sulphuretted hydrogen into the respective sulphurets of arsenic and iron, the former of which is entirely volative, leaving pure sulphuret of iron.

Arsenic, or any of its compounds, in combination with *tin*, may be completely volatilized as sulphuret of arsenic, while the tin remains fixed in the form of sulphuret, and may be entirely converted into the peroxide by subsequently heating to redness in an open crucible.

*On a new compound of boracic acid with soda, and on the probable mode of production of boracic acid in nature.**—The known combinations of boracic acid with soda are restricted to the following three, NaO, BO_3; $NaO, 2\,BO_3$ and $NaO, 6\,BO_3$. Dr. Bolley has supplied a missing member of this series, viz., the salt represented by the formula:

$$NaO\ 4\,BO_3,$$

by boiling together solutions of sal-ammoniac and borax, in the proportion of 2 equivs. of the latter, to one of the former. The process is attended by the evolution of ammonia, and the production of chloride of sodium. When the operation of boiling is continued with a dilute solution until the evolution of ammonia ceases, and the liquid in them evaporated, a deposit of borax is first obtained, the mother-liquor from which crystals yields, on careful evaporation at a low temperature, a crystalline crust on the surface of the liquid, and likewise at the bottom of the evaporating vessel. These crystals are composed according to the formula:

$$NaO_4\ BO_3 + 10\,HO.$$

Dr. Bolley is of opinion that a reaction, similar to that of sal-ammoniac upon borax, is concerned in the production of the natural boracic acid of the Lagoons. He finds that the borates of magnesia and lime, Boracite and Datolile, are similarly effected by sal-ammoniac, and that, if this latter substance preponderates in the mixture, the entire borate is decomposed, boracic acid being liberated, which can then be dissolved by the hot vapours which it always accompanies in the localities of its production, and which according to Payen, likewise contain ammonia.

On two new bodies belonging to the amylic series.†—By distilling equal volumes of crystallized sulphamylate of potash with concentrated bisulphide of potassium, M. Ossian Henry, Jun., has obtained a yellow oily liquid, lighter than water, and which evolves a powerful penetrating odour. This product is the *bisulphide of amyl.* The following equation indicates the mode of its formation:

$$2\,SO_3, C_{10}H_{11}O, KaO + KS_2 = 2(SO_3, KaO) + \underbrace{C_{10}\,H_{11}\,S_2}_{\substack{\text{Bisulphide}\\ \text{of amyl.}}}.$$

Distilled two or three times over chloride of calcium, the bisulphide of amyl yields two products, the first boiling at 210° C (410° F.) is yellowish; and consists almost entirely of monosulphide of amyl; the second, boiling

* Ann. der Chem. und Pharm., LXVIII. 122.

† Ann. de Chim. et de Phy. xxv. 246.

at a temperature between 140° and 260° C. (464° and 500° F.), is a liquid of a fine amber colour, burning with a white flame of great luminosity. This liquid emits a strong and very penetrating alliaceous odour, and possesses a density of 0·918 at 18° C. (65° F.)

Equal bulks of sulphamylate of potash, and sulphocyanide of potassium, both in the form of crystals, intimately mixed and distilled in a large retort, yield a mixture of water and an oily liquid of a yellowish-white colour. This oil is the *sulphocyanide of amyl,* which when purified over chloride of calcium, becomes perfectly colourless. It is lighter than water, and possesses a penetrating alliaceous odour. The liquid begins to boil at 170° C. (338° F.), and the temperature rises as high as 260° C. (500° F.) It burns with a white smoky flame, and its density at 21° C. (68° F.) is 0·905.

The following equation exhibits its composition and mode of production:

$$SO_3, C_{10} H_{11} O, KaO + C_2 NS, KaS = 2(SO_3 K Oa) + \underbrace{C_{12} H_{11} NS_2}_{\text{Sulphocyanide of amyl.}}.$$

Or the sulphocyanide of amyl may be represented as follows:

$$\underbrace{C_2 NS}_{\text{Sulpho-cyanogen.}} + \underbrace{C_{10} H_{11} S}_{\text{Sulphide of amyl.}}.$$

The density of the vapour of sulphocyanide of amyl was found at 6·33, although, according to theory, it should only be 4·504,

When the bisulphide or sulphocyanide of amyl is boiled with pure nitric acid, diluted with a third of its weight of water, and the product is saturated with carbonate of baryta, a salt of sulphamylolic acid is obtained, corresponding to the sulpholetholic and sulphometholic acids.

The following equation exhibits the composition and mode of formation of this salt from the bisulphide of amyl:

$$C_{10} H_{11} S_2 + NO_5, HO = C_{10} H_{11} S_2 O_5 + HO = \underbrace{C_{10} H_{12} S_2 O_6}_{\text{Sulphamylolic acid.}}.$$

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*On the conversion of malic into succinic acid.**—M. Piria has shown that asparagine may be viewed as the amide of malic acid, and that it may be converted by fermentation into succinate of ammonia. The intimate relation of asparagine to malic acid has received additional proof, at the hands of M. Dessaignes, by the metamorphosis of the malic acid contained in malate of lime, into succinic acid.

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* Ann. de Chim. et de Phy. xxv. 253.

The malate of lime obtained by the process of Liebig, from the berries of the mountain ash, was left exposed below the surface of water to the ordinary temperature of the air. In the course of some months, the upper portion of the water was observed to contain a mucilaginous substance, while crystals of carbonate of lime coated the sides of the vessel. As the temperature rose during the summer months, a crust of very fine prismatic crystals was observed on the surface of the malate of lime, which, after purification, were found to consist of pure succinic acid.

*Examination of the oils expressed from the seeds of white and black mustard.**—The acids contained in the oils expressed from the seeds of *Sinapis alba,* and *nigra,* are only known as combinations of oxide of glyceryl, they have never yet been isolated. Mr. Darby has obtained, by the usual methods, from the fat oil of white mustard, an acid, which he terms *Erucaic acid,* and which is nearly allied to the *Behenic acid* of Völker.

The composition of the Erucaic acid is expressed by the formula.

$$C_{44}\, H_{42}\, O_4.$$

The acid melts at a temperature of 34° C (93·5 F.); it is deposited in white needles from solution in alcohol. The salts of silver, lead, and baryta were examined, and their composition is expressed by the general formula:

$$C_{44}\, H_{41}\, O_3,\ MO.$$

There appears to be another acid associated with Erucaic acid in the oil, the lead-salt of which is soluble in ether, and for the baryta compound of which, the author has deduced the following formula:

$$C_{38}\, H_{36}\, O_4,\ BaO.$$

The composition of this acid is, therefore, different from that of the oleic acid contained in the non-siccative oils, the composition of the baryta-salt of which is expressed by the formula:

$$C_{38}\, H_{33}\, O_3,\ BaO.$$

The oil of black mustard was found to contain three acids, viz., Stearic acid, Erucaic acid, and a liquid fatty acid, which appeared to be identical with the latter acid, described as contained in the oil of white mustard.

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* Ann. der Chem. und Pharm. LXIX. 1.

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February 19, 1849.

The President in the Chair.

M. Claudet presented a portrait of Dr. M. Faraday, taken from a Daguerreotype.

Messrs. Edward J. Chapman and John E. Mayer, were elected Members of the Society.

The following papers were read:

IX.—*An account of some experiments with Voltaic Couples.*

By Mr. Richard Adie, *Liverpool.*

In continuing the experiments submitted last year for the consideration of the Chemical Society, in which I sought to show that a metallic oxide acted as a negative element to bright portions of the metal from which such oxide was derived, I formed a voltaic couple with two similar pieces of zinc, one of which was amalgamated, while the other possessed a clean-scraped metallic surface. When this couple was connected in the usual manner with a delicate galvanometer and immersed in oxygenated water, I found it easy to obtain the voltaic current at pleasure, either from the amalgamated surface as the positive, or from the scraped surface as the positive element.

The plates were immersed in the water and allowed to remain for some time till the galvanometer, in connection with them, fell to near zero. The amalgamated plate was then taken out and the surface wiped clean; on re-immersion, the galvanometer immediately indicated that the bright amalgamated surface was positive to the other which had remained for some time in the water, and was slightly oxidized.

Again, allowing a space of time for the galvanometer to return near to zero, the zinc plate with a scraped surface was removed and again cleaned; when put into the water, the galvanometer showed that its surface was positive, while the amalgamated surface had now become negative, the reverse of what it was in the first trial. These experiments were repeated with uniform results, the sole condition which regulated the direction of the voltaic current being the state of the surfaces of the pieces of zinc with reference to oxidation. Unless care was taken, however, to keep the amalgamated surface untouched, I generally found it acting as the positive plate, a result to be expected from the circumstance of the amalgamation of the metal rendering the oxide formed on its surface far more easily removeable than the oxide formed on the surface of unamalgamated zinc.

From these experiments, the object of amalgamating zinc surfaces in voltaic batteries would appear to be to prevent the formation of oxide of zinc on the positive side, where it would act as a negative element, and waste a portion of the power of the battery in generating local currents. In oxygenated-water batteries the metallic oxides are removed from the surfaces of the plates by mechanical means only, there being no acid present to remove them in the form of soluble salts; but in batteries where acids are used, the oxides are removed by combining with part of the acid to form soluble salts. In this case, I presume that amalgamating has still the same kind of action which we find exerted in the oxygenated-water battery, namely, that the particles of the oxide to be combined with the acid are more feebly attached to the amalgamated metallic surface, than to the same surface unamalgamated, and are consequently more readily dissolved.

The usual explanation given of the advantage resulting from amalgamated zinc is, I believe, that it prevents impurities in the zinc from forming local actions, but I apprehend that with the purest zinc, a coating of oxide on its surface, will in an oxygenated-water battery, have greater influence in destroying its positive action than any of the metals found associated with common zinc as impurities.

In continuing the experiments in which pure specimens of metals were enclosed with distilled water in hermetically sealed glass tubes, and where I had found that iron possessed the power at ordinary temperatures of slowly decomposing water, generating hydrogen, I prepared by voltaic action, specimens of antimony, bismuth, lead, and tin, and placed portions of each of these in test-tubes, with pure water; the tubes were afterwards hermetically sealed, the greatest pains having been taken to expel absorbed air from the water by ebullition. In none of these tubes could I discover the slightest evidence of the decomposition of the water. The tubes were then removed to a sand-bath, where they were maintained for two months at a temperature of 100° Fahrenheit, above the ordinary temperatures of the weather, without any of them showing an increase of internal pressure through the generation of hydrogen.

The first three of these metals are held by chemists to be incapable of decomposing water at any temperature, hence it was not to be expected that, like iron, they should possess a slow power of decomposing water; but having found that when they were formed into the positive elements of voltaic couples excited by water in a rapid state of ebullition, the attached galvanometer always indicated a decided action, I felt desirous to try carefully whether the effect could be due to a decomposition of the water. As no evidence of this kind could be obtained from these experiments, it appeared to me, that the action of such voltaic arrangements must be explained on the principle that water, boiling in the atmosphere, always contains some portion of absorbed air, and that it is the oxygen of this air which excites the couple.

A plate of copper associated with one of platinum, and attached to a delicate galvanometer, gave a perceptible action when excited by boiling water: when the plates were at the surface the action was greatest; but when these were placed beneath the surface of the water, there was still decided action. At a depth of 8 inches below the surface a voltaic current was generated, which, according to the above view of the action of such a couple, could only arise from a portion of atmospheric air reaching the plate.

X.—*On the Quantitative Separation of Magnesia, and of the oxides of Nickel, Cobalt, and Zinc, from Potash and Soda. By* Henry Watts, B.A., F.C.S., *Assistant in the Birkbeck Laboratory, University College, London.*

The separation of magnesia from the fixed alkalis is well known to be attended with considerable difficulty. The method given in Rose's Analytical Chemistry,[*] consists in converting the mixed salts into sulphates, adding acetate of baryta in excess to remove the sulphuric acid filtering; converting the acetates of baryta, magnesia, and the alkalis in the filtrate into carbonates by ignition—then digesting in water, and filtering again to separate the alkaline carbonates from the insoluble carbonates of baryta and magnesia. The magnesia and baryta are then separated by means of sulphuric acid. This method is very troublesome and complicated; and after all, does not give very accurate results.

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[*] Dr. Normandy's Translation, vol. II. p. 43.

An easier method is to make use of baryta-water, which precipitates magnesia, leaving the alkalis in solution, and then to remove the excess of baryta either by sulphuric acid, or by carbonate of ammonia. This method is unobjectionable when only the alkalis are to be quantitatively determined; but if the quantity of magnesia is likewise to be estimated, a great deal of trouble is occasioned by the formation of carbonate of baryta, which always takes place more or less during the filtration and washing, whatever pains we may take to exclude the air. The magnesia and baryta have then to be separated by sulphuric acid; and this involves the necessity of expelling a considerable excess of sulphuric acid by heat, which is a troublesome process.

To obviate these difficulties, I have devised the following process, which is nothing more than a particular application of a method in very general use. It consists in precipitating the magnesia by a known weight of carbonate of soda, using a considerable excess; then boiling and filtering; treating the filtrate with a slight excess of acid; evaporating to dryness, and igniting the residue to render it neutral; weighing the neutral salt thus obtained; and making the proper correction for the quantity of soda-salt introduced.

The mode of conducting the process will be best understood by the following examples:

Twenty-five grains of sulphate of magnesia and potash, in well-defined crystals, were dissolved in water, and the liquid was mixed with solution of 10 grains of perfectly anhydrous carbonate of soda. The mixture, which was strongly alkaline, was then boiled for half-an-hour, the water being renewed as it evaporated. This continued boiling is essential to the complete separation of the magnesia. The carbonate of magnesia was collected on a filter, washed with boiling water, then dried and ignited. The quantity of magnesia thus obtained was 2·555 grains; by calculation it should be 2·557.

The filtrate, which contained sulphate of potash, sulphate of soda, and excess of carbonate of soda, was then slightly acidulated with sulphuric acid, to convert the carbonate into sulphate, *so that* *sulphuric acid should be the only acid present.* The liquid was lastly evaporated to dryness in a porcelain crucible, and the residue strongly ignited to render the sulphates *neutral*; carbonate of ammonia being added to remove the last portions of the excess of acid. The residue gave:

Sulphate of potash + sulphate of soda = 24·015 gr.

Now it must be remembered, that 10 grains of dry carbonate of soda were introduced at the beginning of the process; and 10 grains of carbonate yield 13·4 grains of anhydrous sulphate. Deducting this from the weight of the mixed sulphates, we have 10·615 grains of sulphate of potash, which corresponds to 5·73 of potash. The calculated quantity is 5·84.

In a second experiment, conducted in the same manner, the quantity of magnesia was 2·56, and that of potash, 5·77.

The following table contains the results of the two experiments calculated to 100 parts, and likewise the mean of the two. The fourth column gives the theoretical quantities, according to the formula: $KO, SO_3 + MgO, SO_3 + 6 HO$; and the last column gives the differences between the third and fourth. The quantities of sulphuric acid and water of crystallization were likewise determined by the usual methods, in order to prove that the salt was of definite constitution.

	I.	II.	Mean.	Calculation.	Difference.
Magnesia .	10·24	10·22	10·23	10·23	0·00
Potash . .	23·08	22·92	23·00	23·36	0·36—
Sulphuric acid	39·40	39·76	39·58	39·68	0·10—
Water . .	26·96	26·92	26·94	26·73	0·21 +
	99·68	99·82	99·75	100·00	

It will be seen from this, that the process is capable of affording very good results. To ensure accuracy, however, it is absolutely necessary that the solution, after the carbonate of soda has been added to it, be well boiled for at least half-an-hour. The object of this continued boiling is to decompose a difficultly soluble double carbonate of soda and magnesia, which is formed on the first addition of the alkaline carbonate.* The carbonate of soda must likewise be added in considerable excess; otherwise, the precipitation will not be complete. The precipitate of carbonate of magnesia must be washed with boiling water, and the washing not too long continued; for the carbonate is not completely insoluble. The washing should be discontinued as soon as the wash-water ceases to give a distinct alkaline re-action; when this takes place, the water begins to dissolve the carbonate of magnesia.

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* Vide Rose, Normandy's Translation, II. 35.

When, as in the above examples, the quantity of magnesia can be approximately estimated beforehand, it is easy to calculate the quantity of carbonate of soda required to precipitate it; considerably more than that quantity should, however, be used. But if no such estimate can be formed—and this will generally be the case—a certain quantity of the carbonate of soda may be weighed out, and then added in small portions at a time, till the liquid becomes strongly alkaline. The residue may then be weighed, and the difference of the two weighings will give the quantity used for the precipitation. When a quick approximation is desired, rather than a very accurate result, a solution of known strength may be used, and the quantity determined by a graduated measure. But where great accuracy is an object, the method of weighing is much to be preferred. Great care should, of course, be taken, that the carbonate of soda is absolutely pure and anhydrous. The best mode of preparing it is to ignite the bicarbonate or sesquicarbonate.

In the above examples, the magnesia and alkali were in the form of sulphates. If they are in the form of chlorides, the determination of the alkali will be easier; because the excess of hydrochloric acid is more easily driven off than that of sulphuric acid. If they are in the form of nitrates, or if two or more acids are present, it is best, after separating the magnesia, to add sufficient sulphuric acid to convert the whole into sulphates.

When both potash and soda are present, the best plan will be, after precipitating the magnesia, to convert the alkalis into chlorides, which may always be done; then determine the total weight of the alkaline chlorides; deduct the weight of chloride of sodium equivalent to the carbonate of soda used; and lastly, estimate the quantity of chloride of potassium in the usual manner by precipitation with bichloride of platinum.

The same method is applicable to the separation of nickel, cobalt, and zinc from the fixed alkalis. The usual mode of effecting this separation is by means of sulphide of ammonium. But this method, though practicable, is attended with very great difficulties; for the sulphides of these metals are, to a certain extent, soluble in excess of sulphide of ammonium; and if an excess of this reagent be not used, and the precipitate not washed with water containing it, the precipitate oxidizes, and is converted into a soluble sulphate, which runs through the filter.

The following examples will show that the method of precipitation with a known weight of carbonate of soda, gives results as accurate as those obtained with the magnesia-salt. I omit the details of the process, as they are exactly similar to those above described. The quantities of sulphuric acid and water are likewise given, for the same reason as in the former case.

Sulphate of zinc and potash, $ZnO, SO_3 + KO, SO_3 + 6\ HO$

	Exp.	Calculation.	Difference.
Oxide of zinc . .	18·08	18·44	0·36—
Potash . . .	21·08	21·22	0·14—
Sulphuric acid . .	35·88	36·06	0·18—
Water . . .	24·73	24·28	0·43+
	99·77	100·00	

Sulphate of nickel and potash, $Ni\ O, SO_3 + KO, SO_3 + 6\ HO$,

	Exp.	Calculation.	Difference.
Protoxide of nickel .	17·12	17·16	0·04—
Potash . . .	21·52	21·55	0·03—
Sulphuric acid . .	36·35	36.62	0·27—
Water. . . .	24·96	24·67	0.29+
	99·95	10·000	

The same precautions are necessary as in the case of magnesia, viz: to use a considerable excess of carbonate of soda, boil for a long time, wash with boiling water, and not too long.

The examples above given are sufficient to illustrate the method. I have caused it to be tried in a great number of instances by pupils working under my direction in the laboratory of University College. The results are always satisfactory when due attention is paid to the precautions above specified. I now lay it before the Chemical Society, in the hope that it may contribute something towards the removal of an acknowledged difficulty in analysis.

XI.—*On the Composition of Mesitilole, and some of its derivatives.*

By DR. A. W. HOFMANN.

We are indebted to Sir Robert Kane for the investigation of an interesting class of compounds, arising from the decomposition of acetone.* The general result of these researches was the exhibition of a remarkable analogy in the nature of this body to that of an alcohol.

The original formula for acetone, as resulting from Dumas' and Liebig's analyses, was:

$$C_3\,H_3\,O,$$

representing an equivalent of an acetate, minus an equivalent of a carbonate; a formula which, subsequently, when Dumas determined the density of the vapour of this liquid, was doubled, on the supposition that its equivalent corresponded to 4 volumes of vapour.

The products of decomposition of acetone, afforded an additional support to the formula:

$$C_6\,H_6\,O_2,$$

as representing the equivalent of this body, which, according to the experiments of Kane, we have to consider as the hydrated oxide of a compound radical, mesityl, analogous to methyl, ethyl, and amyl:

$$HO,\,C_6\,H_5\,O.$$

In fact, Sir Robert Kane succeeded in isolating the oxide of this radical, as also in combining it with sulphuric and phosphoric acids, and in preparing the chloride and iodide(?) corresponding to the oxide. He, moreover, obtained a liquid hydrocarbon, which he described under the name of mesitilene (mesitilole), and which he considered as representing, in his new series, the olefiant gas of common alcohol.

So far the analogy is complete; we may add even, that since that period an acid has been discovered which, in the mesityl-series, would correspond to the acid terms of the other alcohols. We know that all true alcohols, by losing two equivalents of hydrogen, and assuming two equivalents of oxygen, pass into a class of acids of which formic, acetic, and valerianic acids are familiar instances. Now *acrylic acid* (acronic acid, Berz.), which Prof. Redtenbacher discovered among the derivatives of glycerin, stands to acetone exactly in the relation which exists between common alcohol and acetic acid.

$$\underbrace{C_4\,H_6\,O_2}_{\text{Alcohol.}} - H_2 + O_2 = \underbrace{C_4\,H_4\,O_4}_{\text{Acetic acid.}}$$

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* "On a series of combinations derived from Pyroacetic Spirit," Dublin, 1838.

$$\underbrace{C_6\,H_6\,O_2}_{\text{Acetone.}} - H_2 + O_2 = \underbrace{C_6\,H_4\,O_4}_{\text{Acrylic acid.}}$$

Acrylic acid has not yet been prepared from acetone, which, when subjected to oxidizing agents, is converted into acetic and formic acids; but if we consider the great facility with which, according to Redtenbacher's experiments, acrylic acid is itself converted into these two acids, we may still, perhaps, hope to arrive at this result by a judicious selection of the proper oxidizing agent.

These observations sufficiently prove that acetone exhibits, in a remarkable manner, the characters of an alcohol; nevertheless, our views respecting the nature of this compound appear to be by no means settled. Indeed, the progress of science has not failed to raise a series of objections to the opinion, which, at the time of Sir Robert Kane's experiments, appeared most probable.

The extreme instability of the mesityl compounds, at once distinguishes this group of bodies from the derivatives of the regular alcohols, from which it differs, moreover, in the ratio of the carbon and hydrogen equivalents. The impossibility of reproducing acetone from these derivatives, and the difference in the constitution of sulphomesitylic and sulphovinic acids, likewise appeared to discountenance the reception of acetone into the group of well-established alcohols. The former of these objections has lost some of its weight, since, in the cyanides of the alcohol-radicals, we have become acquainted with a class of alcohol-compounds likewise irreconvertible into the original terms, whilst the latter might, perhaps, be removed by a closer investigation of sulphomesitilic acid and its compounds. Be this, however, as it may, the state of our knowledge respecting the derivatives of acetone, clearly proves that this field has not yet been sufficiently explored.

The following pages contain a small contribution to the history of mesitilole, one of the most interesting among the acetone-descendants, which the researches of Sir Robert Kane have elicited.

To trace the analogy of acetone and alcohol, this chemist naturally directed his attention to the action of dehydrating agents on the former. He found that sulphuric acid readily decomposed acetone, giving rise to a variety of products, among which an oxigenated liquid, oxide of mesityl, according to Kane, the ether of the series, and an oily carbohydrogen (mesitilene), the representative of olefiant gas, are enumerated.

I have repeated this reaction with precisely the same results. On distilling a mixture of 2 volumes of acetone, and 1 volume of concentrated sulphuric acid, a distillate is obtained consisting of an aqueous solution of sulphurous acid, on the surface of which an oily liquid floats, whilst a dark-brown residue remains in the retort. Redistillation of this liquid, after washing with water and drying, evinced at once the compound nature of the oil, which commenced to boil at about 100° C. (212° F.), the boiling-point rising gradually to upwards of 250° C. (482° F.) My attention being chiefly directed to the carbo-hydrogen, which, according to Kane, boils at 135° C. (275° F.), I collected the distillate, passing over between 120° C. (248° F.) and 160° C. (320° F.) separately. On repeatedly distilling this quantity, I, however, soon found that the boiling temperature of the substance I was in search of, was much higher than 135° C. (275° F.); I was consequently obliged to fraction the whole portion, passing over in the first distillation between 120° C. (248° F.) and 200° C. (392° F.) After very numerous distillations a liquid was obtained, boiling pretty constantly between 155° C. (311° F.) and 160° C. (320° F.), which possessed all the properties Sir Robert Kane attributed to his substance, excepting the boiling-point, to the difference in which I have alluded above.

The analysis of mesitilole originally led to the ratio of carbon and hydrogen equivalents—

$$C_3\,H_2,$$

but both the formation of the new body, as being derived from acetone, and the products into which it is converted under the influence of various agents, proved at once that the equivalent of mesitilole was higher. In fact, the preparation of a beautiful crystalline body, by the action of chlorine upon mesitilole, and described by Kane under the name of chloride of pteleyl, compelled him to double the above formula into the following expressions:

Mesitilole . . . . . . $C_6\,H_4$
Chloride of Pteleyl . . $C_6\left\{\begin{matrix}H_3\\Cl\end{matrix}\right\}$

a change which rendered the transformation of acetone perfectly analogous to that of alcohol under the same circumstances:

$$\underbrace{C_4\,H_6\,O_2}_{\text{Alcohol.}}+2H\;SO_4=\underbrace{C_4\,H_4}_{\text{Olefiant gas.}}+2(H\;SO_4\;HO)$$

$$\underbrace{C_6\,H_6\,O_2}_{\text{Acetone.}}+2H\;SO_4=\underbrace{C_6\,H_4}_{\text{Mesitilole.}}+2(H\;SO,\;HO).$$

This formula for mesitilole appeared to be confirmed by the composition of the corresponding bromine- and nitro-compounds:

Bromine-compound . . .	$C_6\left\{\begin{matrix}H_3\\Br\end{matrix}\right\}$
Nitro-compound	$C_6\left\{\begin{matrix}H_3\\NO_4\end{matrix}\right\}$

which, at a later period, were discovered by M. Cahours. The determinations, however, of the density of the vapour of mesitilole, in which M. Cahours had hoped to obtain further support for this formula, gave results which induced many chemists to double again the formula of mesitilole. According to Cahours' density, one equivalent of this substance would contain only two volumes of vapour, whilst all other hydrocarbons, whose equivalents have been ascertained by metamorphoses, have been found to correspond to four volumes of vapour. In fact, we know as yet no exception to this general rule. Olefiant gas, Faraday's gas, Amilole, Cetole, Benzole, Toluole, Naphthalole, &c., substances, the equivalents of which we may consider as fixed both by their origin and by their descendants, all contain invariably four volumes of vapour in one equivalent. These considerations have pretty generally led to the adoption of the following formulæ for the mesitilole series:

Mesitilole	$C_{12}\,H_8$
Chlorine-compound . . .	$C_{12}\left\{\begin{matrix}H_6\\Cl_2\end{matrix}\right\}$
Bromine-compound . . .	$C_{12}\left\{\begin{matrix}H_6\\Br_2\end{matrix}\right\}$
Nitro-compound . . .	$C_{12}\left\{\begin{matrix}H_6\\2NO_4\end{matrix}\right\}$

All the observations which we possess respecting this group appear to find a satisfactory explanation in the assumption of the above formula: there is only one property of mesitilole which does not well agree with this expression, viz.: its boiling-point. In the present state of our knowledge respecting the boiling temperatures of liquids, the discrepancy of the actual boiling-point of mesitilole, and the temperature at which we should expect the ebullition of a liquid represented by the formula

$$C_{12}\,H_8,$$

could not fail to throw some suspicion on the exactness of this expression. If we recollect that the accurate experiments, both of

Mr. Mansfield* and Dr. Kopp,† have fixed the boiling-point of benzole at 80° C. (176° F.), we cannot but be surprised to find a liquid of very similar constitution, containing the same number of equivalents of carbon, and even more hydrogen, boiling at so much higher a temperature. An increase in hydrogen almost invariably depressing the point of ebullition of a compound, we should expect to see mesitilole boiling rather at a lower than at a higher temperature. This circumstance has not escaped Leopold Gmelin, who in his Handbook‡ alludes to this discrepancy. He attributes, however, to the presence of substances possessing a higher boiling-point in the crude product after the action of sulphuric acid upon acetone, that the boiling-point of Kane 135° C. (275° F.) had been observed too high. He mentions likewise that the boiling-point would correspond more closely with a substance of the formula:

$$C_{18}\,H_{12}.$$

We shall see directly that this formula actually represents the composition of mesitilole.

The purification of mesitilole is attended with considerable difficulty and although working on rather a large scale, I have not been able to obtain a perfectly fixed temperature for this substance; but numerous experiments, made both by Mr. Maule and myself, have proved that this point is decidedly between 155° C. (311° F.) and 160° C. (320° F.)

This boiling-point of mesitilole, higher even than had resulted from Kane's experiments, could not fail to invite me to a few experiments with this body, in order to obtain further data for establishing its composition. It appeared by no means impossible that, by the moderate action of decomposing agents, substances might be produced differing in composition from those hitherto obtained, and thus afford a key for the solution of the question.

Action of Bromine on Mesitilole.—The inferior affinity for hydrogen, which distinguishes bromine from chlorine, naturally directed my attention first to this powerful salt-former. Bromine was added carefully, drop by drop, to mesitilole, waiting each time until the heat evolved had subsided, and taking care to keep the hydrocarbon in excess. Mesitilole is thus converted into a white crystalline compound, which was freed from hydrobromic acid by washing with water, in which it is perfectly insoluble. Two or three crystallizations from boiling alcohol render this compound absolutely pure. It presents itself in white needles, which are volatile without decomposition, and are not changed by ebullition with either potash or ammonia.

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* Journ. of the Chem. Soc. Vol. I. 244. † Pogg. Ann. Bd. LXXII. 1 and 223. ‡ Vol. IV.

Analysis gave the following results:

I. 0·3595 grm. of bromine-compound gave:
0·4048 ,, ,, carbonic acid, and
0·0905 ,, ,, water.
II. 0·0223 ,, ,, bromine-compound gave:
0·3540 ,, ,, bromide of silver.

Per-centage composition:

	I.	II.
Carbon . . .	30·70	—
Hydrogen . . .	2·79	—
Bromine . . .	—	66·68

These numbers lead exactly to the composition of M. Cahours' bromine-compound, corresponding with either

$$C_6 \left\{ \begin{matrix} H_3 \\ Br \end{matrix} \right\} \text{ or}$$

$$C_{12} \left\{ \begin{matrix} H_6 \\ Br_2 \end{matrix} \right\}$$

	Theory.		Experiment.
12 equiv. of Carbon . . .	72·00	30·70	30·70
6 ,, ,, Hydrogen . . .	6·00	2·56	2·79
2 ,, ,, Bromine . . .	78·86	66·74	66·68
1 equiv. of Bromine-compound	156·26	100·00	100·17

The properties of the substances likewise prove their identity.

Action of Nitric Acid on Mesitilole.—The action of this acid on the carbohydrogen has been likewise studied by M. Cahours. On treating mesitilole with concentrated nitric acid, he found that a dark yellow oil was produced, which did not present a sufficiently definite character for analysis; by employing, however, a mixture of concentrated nitric and sulphuric acids, he obtained a beautiful crystalline compound, which, when purified by washing with water and repeated crystallizations from alcohol, or by sublimation, exhibited the lustre of metallic silver in a remarkable degree. Analysis proved this compound to be either:

$$C_6 \left\{ \begin{matrix} H_3 \\ NO_4 \end{matrix} \right\} \text{or}$$

$$C_{12} \left\{ \begin{matrix} H_6 \\ 2NO_4 \end{matrix} \right\}$$

My experiments have led me to the same result. By acting either with the sulphuro-nitric mixture, or with fuming acid alone, I have obtained this compound with all the properties which M. Cahours has assigned to it. To his description I need only add, that this substance dissolves with extreme difficulty in boiling alcohol and ether, but is easily purified by crystallization from acetone, in which, as Mr. Maule has found, it readily dissolves.

The following numbers were obtained on analysis:

0·2210 grm. of substance gave:
0·3415 „ „ carbonic acid, and
0·0770 „ „ water.

The per-centage obtained from these numbers closely corresponds with the formula:

$$C_{12}\left\{\begin{matrix} H_6 \\ 2\,NO_4 \end{matrix}\right\}$$

as exhibited in the following table:

	Theory.		Experiment.
12 equiv. of Carbon . . .	72	42·35	42·14
6 „ „ Hydrogen . .	6	3·53	3·87
2 „ „ Nitrogen . .	28	16·48	—
8 „ „ Oxygen . . .	32	37·64	—
1 equiv. of Nitro-compound	138	100·00	

So far my endeavours were attended with but little success. By employing nitric acid of inferior strength, however, I obtained at once a different result.

Mesitilole, when boiled with dilute nitric acid is very gradually attacked, it turns yellow, and loses part of its fluidity. After repeated distillations, it is converted into a yellow oil, showing a tendency to crystallize. This oil is evidently a mixture, and I have not been able to effect a separation, too small a quantity of mesitilole being at my command. By substituting nitric acid of moderate concentration, however, for the dilute acid, a few distillations were sufficient to convert the whole of the mesitilole into the crystalline compound, which presents itself in very fine needles, sometimes several inches in length.

These crystals were washed with water, and finally recrystallized from alcohol: the facility with which they dissolve in this liquid, directly showed me that I had a substance in hand perfectly different from the previous nitro-compound, which it resembles in many other respects, especially in its outward appearance, and its volatility without decomposition.

Analysis gave the following results:

I. 0·2915 grm. of substance gave:
0·5445 „ „ carbonic acid, and
0·1310 „ „ water.
II. 0·2050 „ „ substance gave:
0·3840 „ „ carbonic acid, and
0·0915 „ „ water.
III. 0·2280 „ „ substance gave:
0·4280 „ „ carbonic acid, and
0·1030 „ „ water.

Per-centage composition:

	I.	II.	III.
Carbon	50·94	51·08	51·15
Hydrogen	4·95	4·95	5·01

These numbers closely correspond with the formula:

$$C_9\,H_5\,N\,O_4,$$

which has to be doubled into

$$C_{18}\,H_{10}\,N_2\,O_4 \;=\; C_{18}\left\{\begin{matrix}H_{10}\\ 2\,NO_4\end{matrix}\right\}$$

the expression

$$C_9\,H_6$$

not being reconcileable with the formulæ for the other derivatives of mesitilole.

	Theory.		Experiment.
18 equiv. of Carbon . . .	108	51·42	51·07
10 „ „ Hydrogen . .	10	4·76	4·98
2 „ „ Nitrogen . .	28	13·35	—
8 „ „ Oxygen . . .	64	30·47	—
1 „ „ Nitro-compound	—	—	—
	210·	100·00	

Its subsequent transformation into nitromesidine by Mr. Maule, altogether precluded the necessity of determining the nitrogen in this compound.

The existence of a body of this nature can leave no doubt respecting the true formula for mesitilole. It is evident that a compound of the indicated composition can be derived only from a carbo-hydrogen of the formula:

$$C_{18}\ H_{12},$$

which I consider as the true expression for the equivalent of mesitilole.

The formula of mesitilole, becomes thus identical with that of another carbo-hydrogen which is found among the derivatives of cuminic acid, viz., with cumole. These substances are, however, far from being actually identical. It is only necessary to compare the odour of the two liquids, and their comportment with reagents, in order to remove every doubt upon this head; still these substances, as might be expected, exhibit a remarkable analogy in their physical properties, their boiling points being indeed so near each other, that I do not despair of finding that they are actually identical. The boiling point of mesitilole is, as I mentioned, probably between 155° C. (311° F.) and 160° C. (320° F.); for the boiling temperature of cumole we possess three different observations, respectively announcing it to be at 144° C. (291° F. Gerhardt and Cahours*), 148°C. (299° F. Abel†), and 153°C. (308° F. Gerhardt‡.) It is not impossible that these two liquids boil actually at the same temperature. The compounds, too, arising from the reaction of nitric acid upon cumole present a certain analogy, although here likewise we meet with discrepancies. We have become acquainted with nitrocumole and dinitrocumole, but a trinitro-compound corresponding to trinitromesitilole, for such the nitro-compound first described must henceforth be considered, has not been formed, although M. Cahours subjected both hydro-carbons to exactly the same treatment.

In adopting the new formula for mesitilole we interfere, as is easily seen, in no way with the former results, all the analyses are perfectly correct, they have to be interpreted only in a different manner. There is, however, one observation which, at least according to principles generally admitted, is no longer reconcileable with the atomic composition of our compound. This is the determination of the density of mesitilole as made by M. Cahours. If this determination be correct, —and we have scarcely a better authority in experiments of this kind than M. Cahours,—one equivalent of mesitilole would represent not less than 6 volumes of vapour, a number which has been never observed in any similar case. All the well investigated hydro-carbons, have given hitherto invariably 4 volumes. It is possible that the specific gravity of the mesitilole vapour is subject to similar variations as have been observed with acetic, butyric, valerianic acids, and several other compounds; it is possible, likewise, that an equivalent of mesitilole is actually represented by 6 volumes of vapour, and this anomalous condensation may assist in explaining the difference between the constitution of this body and cumole, which, like the other hydrocarbons, contains only 4 volumes of vapour. Be this, however, as it may, the subject requires further investigation. I have hitherto been prevented repeating the determination of the specific gravity, from not having obtained the hydrocarbon of a perfectly constant boiling-point.

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* Ann. de Chim. et de Phys. 3me Série, I. p. 60.

† Memoirs of Chem. Soc. Vol. III. p. 144.

‡ Ann. de Chim. et de Phys. 3me Série, Tom XIV. 111.

The discrepancies existing between the theoretical and experimental density of mesitilole, when expressed by the formula:

$$C_{18}\,H_{12},$$

compelled me to search for additional support for this formula from other facts. The action of sulphuric acid promised to afford some valuable results with reference to this question.

Action of fuming sulphuric acid on mesitilole.—Mesitilo-sulphuric acid.—Common concentrated sulphuric acid acts but very slowly upon mesitilole; fuming acid dissolves it more readily, a reddish brown liquid being produced, which, when exposed to a moist atmosphere becomes gradually crystalline. The application of heat must be avoided, as it carbonizes the compound with the evolution of sulphurous acid. The evolution of a small quantity of this gas cannot be prevented, even when operating in the cold.

On diluting with water, the brown liquid becomes colourless, and yields, when saturated with an excess of carbonate of lead, a soluble lead-compound, insoluble sulphate of lead remaining. The lead-salt is extremely soluble both in water and alcohol, which renders it difficult of purification. However, by treatment with animal charcoal, and subsequent gradual evaporation, it may be obtained in beautiful white needles of perfect purity; the analysis of this compound gave the following results:

I. 0·3180 grm. of lead-salt gave:
0·1580 „ „ sulphate of lead.
II. 0·2853 „ „ lead-salt gave:
0·1426 „ „ sulphate of lead.

III. 0·3043 „ „ lead-salt gave:
0·3979 „ „ carbonic acid, and
0·1045 „ „ water.

Per-centage composition:

	I.	II.	III.
Lead	33·95	34·15	—
Carbon	—	—	35·66
Hydrogen	—	—	3·81

These numbers lead exactly to the formula:

$$Pb\,C_{18}\,H_{11}\,S_2\,O_6 = Pb\,SO_4,\ C_{18}\left\{\begin{matrix} H_{11} \\ SO_2 \end{matrix}\right\}$$

as exhibited in the following table:

	Theory.		Experiment.
1 equiv. of Lead	103·56	34·22	34·05
18 „ „ Carbon	108·00	35·69	35·66
11 „ „ Hydrogen	11·00	3·63	3·81
2 „ „ Sulphur	32·00	10·58	—
6 „ „ Oxygen	48·00	15·88	—
1 eq. of Mesitilosulphate of lead	302·56	100·00	

The analysis of this lead-salt proves, that the action of sulphuric acid on mesitilole gives rise to a new acid, perfectly analogous to hyposulphobenzolic and hyposulphocumolic acids, with the latter of which, our new compound is identical in composition.

The object of these experiments being only to obtain a further confirmation of the new formula of mesitilole, I have not studied the salts of this acid any further. I may mention, however, that it forms a crystallizable silver salt, which is likewise extremely soluble in water, and readily blackens when exposed to the light.

The formula:

$$C_{18}\,H_{12},$$

which I propose for mesitilol, and which receives further confirmation in the study of *nitromesidine,* a beautiful alkaloid, discovered by Mr. Maule, removes this compound, to a certain extent, from the position originally assigned to it by Kane. We can no longer consider it as the representative of olefiant gas in the mesityl-series, it would much rather correspond to those liquid hydrocarbons which we invariably meet with in the dehydration of both vinic and amylic alcohols, and which, up to the present moment, have not been sufficiently investigated, scarcely anything beyond their isomerism with olefiant gas being established.

I cannot omit here pointing out, that in mesitilole we have another instance of the remarkable tendency, exhibited in certain molecular systems, of uniting three atoms of an inferior order into one compound atom of a higher position. Similar examples we possess in the interesting transition of cyanic acid into cyanuric, in the solidification of chloride of cyanogen gas, and in the transformation of cyanide of ethyl into kyanethine. The natural product, too, which we should expect from the dehydration of acetone, is a substance of the formula:

$$C_6\,H_4,$$

and it is not improbable that this compound is actually formed at a certain stage of the process; under the influence, however, of the powerful agent in the presence of which it is generated, we find it rapidly converted into a compound, containing the triple number of equivalents.

Finally, the correction of the formula for mesitilole affords a striking illustration of the valuable assistance which chemical studies are likely to derive from a more minute investigation of boiling temperatures.

The following table exhibits a synopsis of the mesitilole series:

Mesitilole	$C_{18}\quad H_{12}$
Trichloromesitilole	$C_{18}\left\{\begin{matrix}H_9\\Cl_3\end{matrix}\right\}$
Tribromomesitilole	$C_{18}\left\{\begin{matrix}H_9\\Br_3\end{matrix}\right\}$
Nitromesitilole	$C_{18}\left\{\begin{matrix}H_{11}\\NO_4\end{matrix}\right\}$
Dinitromesitilole	$C_{18}\left\{\begin{matrix}H_{10}\\2NO_4\end{matrix}\right\}$
Trinitromesitilole	$C_{18}\left\{\begin{matrix}H_9\\3NO_4\end{matrix}\right\}$
Mesitilosulphuric acid . . .	$H\,SO_4\,C_{18}\left\{\begin{matrix}H_{11}\\SO_2\end{matrix}\right\}$
Nitromesidine	$C_{18}\left\{\begin{matrix}H_{10}\\NO_4\\NH_2\end{matrix}\right\}$

XII.—*On Nitromesidine, a new Organic base.*

By GEORGE MAULE, ESQ.

STUDENT OF THE ROYAL COLLEGE OF CHEMISTRY.

The new researches upon the composition of mesitilole, pointing out, as they do, the remarkable isomerism of this substance with cumole, the carbo-hydrogen of the cuminic acid series, made it desirable to study some further derivatives of this body, in order to obtain additional evidence in favour of the new formula.

No investigation appeared more appropriate for such a purpose, than that of the comportment exhibited by its nitro-compounds with reducing agents. The formation of new alkaloids, corresponding to the nitro-compounds of mesitilole, which was to be expected, and the simple and accurate methods which we possess of determining the equivalents of such bodies, promised to furnish a series of facts, particularly calculated to control the exactness of the corrected formula. Cumole when treated with nitric acid, gives rise to nitrocumole and dinitrocumole, two substances which have been converted into basic compounds by the action of hydrosulphuric acid. The former compound is converted into *cumidine,* investigated by Mr. Nicholson, whilst the latter yielded to M. Cahours the substance described by him a short time ago, under the name of *nitrocumidine.*

The existence in the mesitilole series of a body, isomeric with nitrocumole being still doubtful, Dr. Hofmann invited me to try the production of a base, corresponding in composition to nitrocumidine.

The following paper contains a description of this new body, which is actually produced without difficulty, and for which I propose the name *Nitromesidine,* instead of Nitromesitilidine, which would be the term for it, constructed according to analogy.

On submitting an alcoholic solution of dinitrocumole

$$C_{18}\left\{\begin{matrix}H_{10}\\2\,NO_4\end{matrix}\right\}$$

to the action of hydrosulphuric acid, the liquid assumes a dark colour, and deposits gradually a large quantity of sulphur, whilst the odour of the hydrosulphuric acid disappears. This treatment is continued for several days, until a fresh quantity of hydrosulphuric acid is no longer decomposed. On the addition of hydrochloric acid, sulphur is again precipitated, which is separated by filtration, when a clear liquid is obtained, which yields a copious yellow deposit, when mixed with a solution of potash or ammonia. This precipitate is nitromesidine in an impure state.

To purify this substance, it is repeatedly dissolved in hydrochloric acid, and reprecipitated by an alkali. In this manner, small quantities of still-adhering sulphur are separated, and the substance gradually assumes a bright yellow colour. One or two crystallizations from alcohol now suffice to render it absolutely pure.

Composition of Nitromesidine.—The following analyses were made on crystallized specimens of pure nitromesidine, prepared at different periods, and dried at 100° C. (212° F.)

I. 0·2861 grm. of substance gave:
0·6309 ,, ,, carbonic acid, and
0·1716 ,, ,, water.
II. 0·2072 ,, ,, substance gave:
0·4561 ,, ,, carbonic acid, and
0·1264 ,, ,, water.
III. 0·2264 ,, ,, substance gave:
0·4967 ,, ,, carbonic acid, and
0·1387 ,, ,, water.

Per-centage composition:

	I.	II.	III.
Carbon . . .	60·14	60·03	59·85
Hydrogen . .	6·66	6·77	6·80

A determination of the nitrogen according to Bunsen's method, gave the following results:

	Level in tube.	Vol. corr.	Level of mercury in trough.	Temp.	Bar.	Vol. at 1m press. and 0°. C.
Mixture of carbonic acid, and nitrogen, moist.	137	136·3	249·5	9·0	779·1mm	89·6606
Dry nitrogen.	19·4	17·2	250·0	9·5	773·5mm	9·362

Ratio of carbon and nitrogen equivalents:

$$89{\cdot}6606 - 9{\cdot}362 : 9{\cdot}362 = 100 :$$

Calculating from the mean per-centage of carbon found (60·01) this ratio leads to 16·3 per cent of nitrogen.

Although this result is not so near as those usually obtained, I mention it as a confirmation of the formula resulting from the above analyses, which is:

$$C_{18}\,H_{12}\,N_2\,O_4, \text{ or } C_{18}\left\{\begin{matrix}H_{12}\\NO_4\end{matrix}\right\}N,$$

as will be evident from the following table:

	Theory.		Mean of experiments.
18 equivs. Carbon . .	108	60·00	60·01
12 ,, Hydrogen .	12	6·67	6·74
2 ,, Nitrogen. .	28	15·55	16·31
4 ,, Oxygen . .	32	17·78	—
1 ,, Nitromesidine .	180	100·00	

Properties of Nitromesidine.—This substance is obtained, when pure, in long needle-shaped crystals of a golden yellow colour. The crystals fuse into a liquid at a temperature below 100^0 C. (212^0 F.) and solidify on cooling into a mass of radiated needles. They are very soluble in alcohol and ether, and also slightly so in water, to which they impart a faint yellow colour. Nitromesidine volatilizes without decomposition at 100^0 C. (212^0 F.) its vapour burns with a bluish flame. Its solutions are neutral to test paper, and have an unpleasant bitter taste.

Compounds of Nitromesidine.—Nitromesidine dissolves readily in acids forming crystalline salts; its basic power is however very feeble, most of its salts are readily changed; all those which I have obtained, with the exception of the platinum double salt, and the phosphate, are actually decomposed by mere contact with water. They are soluble in alcohol, and their solutions possess an acid reaction.

Hydrochlorate of Nitromesidine.—To prepare this salt the base is dissolved in dilute hydrochloric acid, and the solution evaporated. When now allowed to stand, the salt crystallizes in colourless needles. This salt being decomposed by water, the solution was evaporated to dryness on the water bath, and allowed to remain until the free acid was completely expelled. It was then dried at 100^0 C. (212^0 F.)

0·3148 grm. of the salt gave:
0·5716 ,, ,, carbonic acid, and
0·1703 ,, ,, water.
0·1593 ,, ,, the salt gave:
0·1051 ,, ,, chloride of silver.

The above analysis corresponds with the formula:

$$C_{18} H_{12} N_2 O_4 HCl,$$

as the following table shows:

	Theory.		Experiment.
18 equivs. Carbon . .	108·0	49·89	49·52
13 ,, Hydrogen .	13·0	6·00	6·01
2 ,, Nitrogen .	28·0	12·93	—
4 ,, Oxygen . .	32·0	14·78	—
1 ,, Chlorine .	35·5	16·40	16·32
1 ,, Hydrochlorate	216·5	100·00	

Bichloride of Platinum and Nitromesidine.—When an excess of bichloride of platinum is added to a hot saturated solution of the above salt, the liquid, on cooling, deposits the double salt of nitromesidine and bichloride of platinum in groups of yellow crystals. To free the salt from an excess of bichloride of platinum, it was washed with water, and afterwards crystallized from alcohol. To control the formula, and ascertain the atomic weight of the substance, four careful determinations of platinum were made in specimens of the salt prepared at different times.

I. 0·2122 grm. of platinum salt yielded:
0·0544 „ „ platinum.
II. 0·2587 „ „ platinum salt yielded:
0·0661 „ „ platinum.
III. 0·1625 „ „ platinum salt yielded:
0·0410 „ „ platinum.
IV. 0·1806 „ „ platinum salt yielded:
0·0462 „ „ platinum.
V. 0·3358 „ „ platinum salt yielded:
0·3470 „ „ carbonic acid, and
0·1083 „ „ water.
VI. 0·3741 „ „ platinum salt yielded:
0·3838 „ „ carbonic acid, and
0·1167 „ „ water.

These numbers give for 100 parts:

	I.	II.	III.	IV.	V.	VI.
Platinum .	25·63	25·55	25·23	25·58	—	—
Carbon . .	—	—	—	—	28·18	27·97
Hydrogen .	—	—	—	—	3·58	3·46

leading to the formula:

$$C_{18} H_{12} N_2 O_4, HCl, Pt Cl_2,$$

as the following calculated numbers will shew:

			Theory.		Mean of experiments.
18	equivs.	Carbon . .	108·00	27·96	28·07
13	„	Hydrogen .	13·00	3·36	3·50
2	„	Nitrogen . .	28·00	7·25	—
4	„	Oxygen . .	32·00	8·30	—
1	„	Platinum . .	98·68	25·55	25·49
3	„	Chlorine . .	106·50	27·58	—
1	„	Platinum salt	386·18	100·00	

Sulphate of Nitromesidine.—When the base is dissolved in boiling dilute sulphuric acid, the solution deposits, on cooling, white silky crystals of the sulphate. This salt is decomposed by water, the base being separated; its analysis was, therefore, abandoned.

Nitrate of Nitromesidine.—This salt is formed when nitromesidine is dissolved in dilute nitric acid. The solution on being evaporated with an excess of free nitric acid is decomposed when the evaporation reaches a certain point, red nitrous fumes being disengaged, and a red oily product of decomposition remaining.

Tribasic Phosphate of Nitromesidine.—When the base is dissolved in a solution of phosphoric acid the salt crystallizes in leafy crystals of a beautiful lemon-yellow colour. It may be washed with water without decomposition. The salt, after the removal of the free acid, is perfectly pure. A portion of the salt dried at 100° C. (212° F.) gave the following results:

I. 0·2471 grm. of the salt gave:
0·4580 „ „ carbonic air, and
0·1413 „ „ water.
II. 0·3058 „ „ the salt gave:
0·0529 „ „ pyrophosphate of magnesia,

which agree with the following formula:

$$3\ (H\ C_{18}\ H_{12}\ N_2\ O_4),\ PO_8,$$

as is shown by reference to the following numbers:

	Theory.		Experiment.
54 equiv. of Carbon	324·0	50·70	50·54
39 „ „ Hydrogen . .	39·0	6·10	6·35
6 „ „ Nitrogen . . .	84·0	13·14	—
20 „ „ Oxygen	160·0	25·06	—
1 „ „ Phosphorus . .	32·0	5·00	4·86
1 equiv. of Phosphate . .	639·0	100·00	

If a large excess of phosphoric acid be employed, an acid salt is obtained, which appears to contain only one equivalent of nitromesidine.

Products of Decomposition of Nitromesidine.—The small quantity of substance at my command, and the tedious processes requisite to obtain nitromesidine, have prevented my studying, to any great extent, the products of its decomposition.

Action of Bromine and Chlorine on Nitromesidine.—When nitromesidine is brought into contact with bromine, a violent action takes place, and the resulting compound is a dark oily substance. This reaction is interesting, as showing the difference between nitromesidine, and its isomeric compound, nitrocumidine; the latter substance, when acted on by bromine, yielding a crystalline solid.

An alcoholic solution of nitromesidine, when exposed to the action of chlorine, yields a pinkish solid, which is soluble in boiling ether, and from which it separates on cooling.

The reduction of trinitromesitilole by hydrosulphuric acid appeared of great interest, since no nitro-compound containing 3 atoms of hyponitric acid has, up to the present moment, been subjected to such treatment. Trinitromesitilole is very difficult of reduction; I have submitted a considerable quantity of the substance to the action of hydrosulphuric acid for several weeks, and found at the end of that period a very small quantity had been acted on. I have, however, obtained a sufficient quantity of the product to establish the existence of a basic compound, produced from trinitromesitilole, although the small amount of this substance, and the difficulty of obtaining it sufficiently pure, has compelled me to defer its examination to a future period.

March 3, 1849.

The President, in the Chair.

August W. Hofmann, Ph.D., was elected a member of the Society.

The following papers were read:

XIII.—*On the compounds containing Phosphorus and Nitrogen.*

By J. H. Gladstone, Ph.D.

Davy was the first to describe any of the combinations containing both phosphorus and nitrogen, and since his time the subject has engaged the attention of Rose,* Liebig,† and Gerhardt.‡ Whilst the singularity of their composition, and the remarkable stability which could not have been anticipated in such compounds, give them a peculiar interest, there exist great discrepancies between the accounts of them given by different chemists. At the instigation of Professor Liebig, I commenced some time ago an examination of the matters in dispute, and I have subsequently been led to extend my researches. I shall now lay before the Society my investigations upon some of the doubtful points, and I hope shortly to present a second communication upon other compounds, into which the same two elements enter.

When pentachloride of phosphorus is thoroughly saturated with dry ammoniacal gas, a bulky white powder is produced, consisting of chloride of ammonium, chlorophosphuret of nitrogen, and a peculiar substance, which, when thrown upon a filter, and washed for a long time with hot water, is resolved into chloride of ammonium, and a white insoluble powder containing no chlorine in its composition. Wöhler and Liebig, the first discoverers of this latter substance, were led to regard it as the hydrate of the phosphuret of nitrogen bearing the formula N_2 P (2 HO). Gerhardt, on the contrary, assigns to it the composition PH_3 N_2 O_2, being, in fact, phosphate of ammonia, minus five atoms of water $2\ (NH_4\ O)\ PO_5 - 5\ HO = PN_2\ H_3\ O_2$; and, although not containing the elements of amidogen, he terms it phosphamide.

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* Poggendorff's Ann. Vol. xxviii. p. 529.

† Liebig's Annalen, Vol. xi. Part. 2.

‡ Ann. de Chimie, 3me. Sér. Octobre, 1846.

Two methods of preparing the substance from the bulky white powder are given. The one consists in washing it with hot water until no more chloride of ammonium is produced; but as the washing may continue for a fortnight before perfect purity is obtained, this process has the disadvantage of being very tedious. Or it may be boiled alternately with potash and nitric acid, until a portion after being washed, dried, and heated in a tube, gives no sublimate of chloride of ammonium; this process, however, proved very destructive to the substance itself. The plan I found preferable was, first to purify the powder from chlorophosphuret of nitrogen, which is an invariable concomitant, either by dissolving out the latter with ether, or, as is better, by boiling the whole mass in water, when the chlorophosphuret is volatilized along with the steam; and then to keep the substance immersed in water in brisk ebullition for five or six hours. As the liquid containing the solid matter is subject to very violent succussions, it will be found advantageous not only to adopt the usual preventatives, but to place it in a capacious flask, and suspend it over the flame. And as continued boiling exerts a destructive influence upon the new product itself, it is desirable not to protract it beyond the time when the conversion is complete, which may be ascertained as above.

The white powder thus produced shows no disposition to combine with alkalis or acids; it is insoluble in alcohol and oil of turpentine, as well as in water, but when boiled with the latter it is very slowly decomposed, phosphoric acid and ammonia remaining in solution. This decomposition takes place rather more rapidly if caustic potash be present, ammonia being of course in that case evolved. Sulphuric acid has no effect upon it in the cold, but when heated, decomposition ensues, the solid matter entirely disappears, and phosphoric acid and ammonia are found in the solution: no sulphurous acid is evolved during the decomposition, but the solution is dark coloured. The sulphuric acid may be only very slightly diluted in order to obtain this effect. When fused with caustic potash, ammonia is given off, and phosphate of potash formed. ' If heated *per se* in the open air, or even in oxygen gas, it is not burnt, but ammonia is given off, and a new compound remains: this action will be reverted to presently. If the powder thus heated be moist, the elements of water take part in the transformation, ammonia is given off as before, and metaphosphoric acid is found in the tube; but I never obtained, as Gerhardt describes, a complete conversion of the substance into phosphate of ammonia; some dark coloured insoluble matter always remained. Chlorine gas has no effect upon it, either in the cold, or at any temperature insufficient to decompose the substance itself. Although containing both phosphorus and hydrogen, it resists the action of most oxidizing agents. It is not affected by boiling in strong nitric acid, nor by a mixture of sulphuric and nitric acids: when fused with nitre, it is but slowly oxidized; but it deflagrates when heated with chlorate of potash.

This difficulty of decomposition rendered the analysis of the substance, and especially the determination of the phosphorus no easy task. The method followed by Gerhardt, namely, that of igniting the substance with oxide of lead and nitric acid, gave me a result indicating 37·9 per cent of phosphorus, but the mass left in the crucible was not wholly soluble in nitric acid, and I have reason to believe that one of the products of the action of heat is formed, which of course, would completely vitiate the result. Combustion with oxide of copper is quite inadmissible for the same reason. The following estimations, however, were severally obtained by a different method, the substance analyzed being dried in each instance by the heat of a water-bath.

I. 0·4245 grm. of substance, prepared by the boiling process, was fused in a silver vessel with pure hydrate of potash, until all odour of ammonia disappeared. The phosphoric acid was converted into phosphate of baryta, and being estimated in the usual manner was found to be 0·306 grm.

II. 0·2485 grm. of the same, oxidized by means of a mixture of about 1 part chlorate of potash and 3 parts nitre, gave of phosphoric acid, estimated in the same manner, 0·178 grm.

III. 0·267 grm. of the same substance was decomposed by heating with strong sulphuric acid, which was then largely diluted, the sulphuric acid having been removed by means of acetate of lead, the phosphate of lead mixed with oxide was analyzed. This yielded 0·1828 grm. phosphoric acid. This method, however, is subject to several inaccuracies.

IV. 0·2028 grm. of substance prepared by alternate boiling with acid and alkali was first heated *per se*, and the grey powder thus produced was oxidized by fusion with nitrate of potash. The phosphoric acid, estimated by means of baryta salt, was 0·1482 grm.

These numbers give the following results per cent; the equivalent of phosphorus being always taken at 32 on the hydrogen scale.

	I.	II.	III.	IV.
Phosphorus .	32·04	31·83	30·41	32·44

The amount of hydrogen in the substance under examination was easily determined by combustion with chromate of lead.

I. 0·4025 grm. of substance prepared by long washing with hot water, and dried at 100° C., yielded 0·121 water.

II. 0·3435 grm. of substance prepared by the boiling process, yielded 0·1035 water.

III. 0·4385 grm. of the same, dried at a temperature of 140° C. (284° F.), so as to render the presence of accidental moisture impossible, yielded 0·1405 water.

These numbers give the following for 100 parts :

	I.	II.	III.
Hydrogen . . .	3·34	3·35	3·56

These results differ materially from those of both Liebig and Gerhardt.

The amount of nitrogen was determined by conversion into ammonia according to Will's process.

I. 0·3195 grm. of substance prepared by long washing, and dried at 100° C., was burnt with soda-lime, and yielded 0·6835 grm. of reduced platinum.

II. 0·502 grm. of substance prepared by the boiling process, yielded 2·1825 grms. of double salt of platinum and ammonium.

III. 0·443 grm. of the same heated first *per se*, and afterwards fused with pure potash, the gas evolved being in both instances collected in the usual hydrochloric acid apparatus, yielded 1·956 grms. of double salt.

IV. 0·3155 grm. of a fresh sample, prepared by the boiling process, burnt with soda-lime, yielded 1·505 grms. of double salt.

These numbers calculated upon 100 parts give:

	I.	II.	III.	IV.
Nitrogen . .	30·31	27·29	27·69	29·92

It is worthy of remark that this result accords with the number obtained by Liebig, who estimated the nitrogen as a gas, 28·526, &c., a result, however, upon which he placed little reliance.

There is sufficient discrepancy in these numbers deduced from experiment, to show that the substance operated upon, was not perfectly uniform; but as it appears insoluble in any menstruum, and incapable of crystallization, I have been unable to devise any means of purifying it. The results, however, agree sufficiently to place the fact beyond doubt, that the proportions in which the phosphorus, nitrogen and hydrogen are combined is as $P : H_3 : N_2$, but united with a larger amount of oxygen than the two atoms assigned it by Gerhardt. Indeed, the amount obtained by me of each of the elements in question, is far below and quite incompatible with that given by him. The numbers accord most closely with those deduced from the formula $P_2\ H_6\ N_4\ O_9$:

Phosphorus	32·32
Hydrogen	3·03
Nitrogen	28·28
Oxygen	36·36

The real composition of the substance is probably $PH_3\ N_2\ O_5$, with which the majority of the results are not incompatible.

	Calculated.		By experiments from subst. produced by boiling process.		
Phosphorus	32	31·07	32·04	31·83	30·41
Hydrogen	3	2·91	3·35	3·56	—
Nitrogen	28	27·19	27·29	27.69	—
Oxygen	40	38·83	—	—	—
	103	100·00			

This view is strengthened when we consider that, in the formation of the white powder, oxidation must have taken place during some part of the process, as will be evident from the annexed equation; now it is very possible that the oxidation has not been in all instances complete, which will readily account both for the variations in the analytical results, and for their discrepancy with theory.

$$P\ Cl_5\ \&\ 7\ NH_3\ \&\ 2\ HO\ \&\ 3O = 5\ (NH_4\ Cl)\ \&\ PH_3\ N_2\ O_5.$$

The simultaneous formation of chlorophosphuret of nitrogen, throws no light upon this reaction.

As the substance operated upon in all these analyses was dried at a somewhat high temperature, the objection might be urged that the oxidation really took place during that process. It became desirable, therefore, to dry it in some other manner. When left for any length of time between sheets of blotting paper, at the ordinary temperature, it still retains a considerable quantity of moisture. A portion was, therefore, allowed to remain in vacuo over sulphuric acid for seven days; it was then weighed and exposed freely to the air in an oven at the temperature of 100° C. for an hour. No change took place; and upon being heated to low redness in a tube closed at one end, it gave a grey powder, weighing 84·6 per cent of the original substance, a result coinciding (as will be presently seen) with that obtained from it when dried in a water-bath, thus proving that the white powder is identical, whether dried at 100° C. or in vacuo over sulphuric acid, and that the oxidation must be sought for in some earlier part of the process.

BIPHOSPHAMIDE.

The fact that a new substance different in properties from that just described, is produced by the action of heat upon the latter, has already been incidentally remarked. This substance has been named "Biphosphamide;" by Gerhardt, he states that it is formed by the separation of all the hydrogen and half the nitrogen from phosphamide, and has the composition PNO_2. His account of the formation I find to be true, but it is evident that if my determinations of the composition of the original substance be correct, it is impossible that Gerhardt's formula can be the true expression for this new one.

When the substance of which the analysis has just been given, is rapidly heated *per se* to incipient redness, it gives off ammonia, and a gritty grey powder remains. This takes place whether the experiment be conducted in air or oxygen gas, or in hydrogen, carbonic acid, or chlorine; in the case of the two latter gases, volatile ammoniacal compounds being of course formed. To prepare the new body, the substance (*phosphamide*) should be heated either in a narrow tube, closed at one end, or better in a gas containing no oxygen, in order to avoid the partial establishment of a reaction which will be subsequently described.

The proportion of the new substance remaining, I found to be as follows:

I. 0·211 grm. of the white powder dried in a water bath, heated in a test tube, yielded 0·176 grm. of the new substance.

II. 0·365 grm. of the one, heated in the same manner, yielded 0·3055 grm. of the other.

III. 0·2028 grm. heated in hydrogen gas, yielded 0·1695 grm.

IV. 0·2025 grm. of a separate preparation heated in a stream of carbonic acid, yielded 0·1675 grm.

These figures show that the new substance forms respectively 83·4, 83·7, 83·6, and 82·7 per cent of the original; thus coinciding with the number deduced from theory, supposing $PN_2 H_3 O_5$ to lose one equivalent of ammonia, and become PNO_5, viz. 83·5. The last of the four results rather favours the view, that the original substance has the composition $P_2 H_6 N_4 O_9$, and the new one that of $P_2 N_2 O_9$, in which case the reduction would be to 82·9 per cent.

Two attempts were made to estimate the amount of ammonia evolved, by collecting the gas in an ordinary hydrochloric acid apparatus, affixed to the little tube in which the substance was heated; but the last portions of ammonia always come off with difficulty, and it appeared that the slight pressure exerted by the liquid in the apparatus was sufficient to prevent the alteration being complete. The amounts remaining in the tube were respectively 86·8 and 86·4 per cent, the loss being therefore 13·2 and 13·6 per cent, and the ammonia actually in combination with the hydrochloric acid amounted to 10·9 and 12·8 per cent respectively. This discrepancy is explained by the fact, that upon the first heating of the substance, a little water is always given off; this I found to take place even when the original substance had been exposed for some time to a temperature above 100° C. so that it could not arise from accidental moisture. In the first instance, the water was collected in a tube filled with sticks of caustic potash, which was placed between the hydrochloric acid apparatus, and the tube in which the experiment was conducted: the amount was 1·8 per cent. In the second experiment, the quantity, although not directly estimated, was evidently much smaller.

Analysis confirmed the view taken of the composition of this substance.

I. 0·1695 grm. deflagrated with nitrate of potash, and the phosphoric acid estimated by means of baryta, yielded 0·1432 grm. of the acid.

II. 0·2262 grm. burnt with soda lime, yielded 0·589 grm. of double chloride of platinum and ammonium.

A portion mixed with chromate of lead and heated, produced no water; therefore it may be concluded that the substance does not contain hydrogen.

These figures calculated upon 100 parts give the annexed, which will be found to be somewhat higher than those deducible from the formula PNO_5, though not so high as those required by $P_2N_2O_9$.

	Calculated.	Experimental.		Calculated.
	PNO_5	I.	II.	$P_2N_2O_9$
Phosphorus . .	37·21	38·82	—	39·03
Nitrogen . .	16·28	—	16·33	17·07
Oxygen . .	46·51	—	—	43·90

This substance, like that from which it is derived, is insoluble in all the ordinary menstrua, nor does it form compounds with acids or alkalis. When boiled with a solution of potash it is unaffected; when fused with the solid hydrate, ammonia is evolved, and phosphate of potash formed. It is decomposed by boiling sulphuric acid, but not without difficulty, the solution becoming very black, and a little sulphurous acid being evolved. It resists the oxidizing action of strong nitric acid, but deflagrates when fused with nitre. When subjected to a full red heat it fuses, and upon cooling remains as a black vitreous mass; but even though the experiment be conducted with free access of air, as for instance, on a piece of platinum foil, no combustion or other alteration takes place; the weight remains the same.

If before heating the substance it be moistened with a little water, a transformation into phosphoric acid and ammonia takes place, as with the compound from which it is derived, but in this case also I did not find the change to be complete. Chlorine has no action upon this body; if it be heated in a current of that gas, the weight remains the same. If mixed with iodine or sulphur and heated, the metalloid sublimes, without producing any change. If heated in a stream of hydrosulphuric acid gas, the grey powder assumes a dark semi-fused sticky appearance, and increases somewhat in weight. For this experiment, the gas should be made from sulphide of antimony, in order to avoid the admixture of hydrogen, which has a widely different effect upon the substance under examination. If the powder be heated in a current of this latter gas, a peculiar action is soon instituted: ammonia is given off, and subsequently white fumes pass along the tube in which the experiment is conducted, consisting of phosphoric, or perhaps phosphorous acid mixed with spontaneously inflammable phosphuretted hydrogen; in the mean time, a red sublimate, apparently impure oxide of phosphorus, is formed in the tube, and sometimes a small quantity of water condenses. In one instance, I obtained no sublimate, and no phosphuretted hydrogen was evolved, but much phosphoric acid and water were produced.

This action may continue for a long time, but a portion always remains which resists the further influence of the hydrogen. It is of a dark brown colour, insoluble in water, and combines neither with acids or alkalis; it is slowly decomposed by strong nitric acid, yielding phosphoric acid; when fused with caustic potash some ammonia is evolved, thus proving that the nitrogen has not wholly departed, but it is not rendered wholly soluble by this fusion with potash; when heated with chromate of lead no water is formed thus showing that hydrogen has not entered into its composition.

This is not the only conversion which "phosphamide" undergoes by the influence of heat. If atmospheric air have free access to it while the temperature is slowly raised, a totally different result is obtained. At about 150 C. (302° F.) the substance begins to evolve ammonia, and to increase in weight; if the heat be now maintained at any point between that, and perhaps one hundred degrees (C.) higher, for half-an-hour, or even longer, ammonia will continually be evolved, and the weight will constantly increase. The resulting substance has a somewhat dark appearance, and is resolved by water into two portions—the one soluble,—the other insoluble and identical with the grey powder formerly described. The proportionate amount of the two depends upon the degree of access which air has to the substance during the process, and also upon the rapidity with which the heat has been raised. It is evident that the mere amount of increase in weight will afford no foundation upon which to calculate the amount of oxygen absorbed. In one instance, however, when there was very little of the grey powder produced, the increase was found to be as much as 22·8 per cent. As ammonia had been given off during the whole process, the oxygen absorbed must have been very considerable. The aqueous solution contained merely a trace of free acid: when evaporated to dryness it gave a crystalline mass, consisting, in a great measure, of phosphate of ammonia. No portion was soluble in alcohol.

PHOSPHURET OF NITROGEN.

When the compound produced, by saturating chloride of phosphorus with ammoniacal gas, is heated to redness, or when the substance formed by passing the vapour of terchloride of phosphorus through a tube filled with pure chloride of ammonium, at a temperature nearly sufficient to volatilize the salt, is washed and heated to redness, a substance is produced, which Rose named *phosphuret of nitrogen,* believing it to have the composition PN_2, although he never succeeded in obtaining it absolutely free from hydrogen. Gerhardt, however, regards it as a substance of the composition PHN_2, (*phospham*) mixed with a quantity of his "biphosphamide," which contains none of the element in question, and as the amount of hydrogen required by such a formula is 1·64 per cent., and that given in the recorded experiments varies about 0·7 per cent., it is evident that we must suppose the "phospham" to be contaminated with about its own weight of "biphosphamide." He affirms that the admixture of this latter substance is to be expected, *a priori*, from the extreme avidity for moisture which both chlorides of phosphorus display, and the impossibility of keeping them in a perfectly dry atmosphere during the whole of the process. Now it remains yet to be shown that "biphosphamide," *i.e.*, my grey powder, can be formed from oxychloride of phosphorus, phosphorus, or phosphoric acids, which are the veritable products of the action of water upon the two chlorides in question; and in the total absence of all positive proof, we are not without evidence to the contrary. For, if the statement of Rose be correct, that phosphuret of nitrogen is decomposed, and rendered wholly volatile by sulphuretted hydrogen, it is impossible that it should be composed, in a great measure, of this grey powder, which I find not to be so affected, and the same remark will hold good in reference to the action of hydrogen, though this is, I conceive, not so conclusive as the other. When it is remembered that the amount of hydrogen found in the analysis of this substance is always very small, and, in fact, in one of Rose's determinations, did not exceed 0·25 per cent., I see no sufficient ground for doubting the correctness of the formula given by that chemist.

There are no direct means for ascertaining the composition of the chlorinated product from which the "phosphamide" is derived, owing to the impossibility of obtaining it in a pure state. Gerhardt assigns to it the formula, $PCl_3\ N_2\ H_4$, calling it "chlorophosphamide;" but as the theoretical grounds upon which he based his conclusion prove to be incorrect, this is probably not the true expression; though I must add, such a view is not incompatible with my results.

I subjoin, in a tabular form, what I conceive to be the true composition of those two compounds of phosphorus and nitrogen, which I have minutely examined, together with the formula assigned by Rose to his "phosphuret of nitrogen." I have not altered the names given to these substances by former investigators, although they are manifestly inappropriate, since I am not satisfied respecting their theoretical constitution, and any new name must involve a theory.

Gerhardt's name.	Other appellations.	Composition.
Phosphamide.	Liebig's hydrate of phosphuret of nitrogen.	$PN_2\ H_3\ O_5$
Biphosphamide.	" Gray powder."	$PN\ O_5$
Phospham.	Rose's phosphuret of nitrogen.	PN_2

NOTE.—In drying this substance, I repeatedly witnessed an electrical phenomenon. It was my practice to place a portion of the powder on a watch-glass, and expose it thus in an oven, at a temperature of 100° C. When thoroughly dried, if the watch-glass be removed from the oven, and the finger drawn across the bottom of it, the powder will become excited, and portions of it will, in all probability, be projected over the sides of the glass. If the watch-glass be covered by another of the same size, as was my practice for weighing the substance, and either the upper or under one be rubbed, the phenomena of attraction and repulsion are beautifully seen. Of course, the watch-glass may be rubbed with silk, woollen cloth, dry wood, or any other electric, with a similar effect.

XIV.—*On Phospho-cerite, a new Mineral containing Phosphate of Cerium; with Observations on the Separation of Cerium, Lanthanum, and Didymium. By* HENRY WATTS, B.A., *Assistant in the Birkbeck Laboratory, University College.*

The mineral which forms the subject of the following communication, is contained in the cobalt ore of Johannisberg, in Sweden; and remains as a residual product, when the ore, after calcination, is treated with hydrochloric acid, for the purpose of extracting the cobalt. It does not form more than one-thousandth part of the whole substance. It was discovered some years ago, by Mr. Ollive Sims,* of the Staffordshire Potteries, and sent to Professor Graham, to whose kindness I am indebted for the opportunity of examining it. Mr. Sims believes that it likewise exists in the cobalt-ore of Tunaberg.

The substance in question, is a greyish-yellow crystalline powder, intermixed with a small quantity of dark purple crystals of another substance. The purple crystals are strongly attracted by the magnet, and, with a little care and patience, may be easily separated from the others by moving a magnet through the entire mass.

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* Transactions of the Chemical Society, vol. I. p. 7.

The yellow particles, when examined by a powerful microscope are found to consist of crystals belonging to the square prismatic system. Two forms appear to occur with tolerable frequency: one, a square-based octohedron; the other, a square prism, with four-sided pyramidal summits.

The specific gravity of these crystals is 4·78; their *degree of hardness*, is intermediate between 5·0 and 5·5.*

The dark-coloured magnetic crystals are perfectly opaque; and when viewed by the microscope, exhibit the form of the rhomboidal dodecahedron, which is one of the crystalline forms of magnetic iron ore: some of them, however, have a pyramidal shape. They are soluble in hydrochloric acid, the solution containing iron in the form of ferroso-ferric oxide ($Fe_3 O_4$), and cobalt. The presence of the latter metal is also easily recognised by the blow-pipe.

The yellow transparent crystals evidently constitute the essential part of the mineral: they were analysed as follows.

QUALITATIVE ANALYSIS.

A quantity of the yellow crystals having been reduced to a very fine powder, so as completely to break up the crystalline structure, the powder was subjected to the action of various solvents. It is insoluble in water. Strong nitric acid, at a boiling heat, dissolves it sparingly; strong hydrochloric acid, somewhat more readily. But the best solvent for this substance is concentrated sulphuric acid. A quantity of this acid having been diluted with water to free it from sulphate of lead, the powder was boiled in it till the whole was reduced to a pasty mass. This was left to cool, water poured upon it, and the whole left to stand for a few minutes. The greater part of the solid matter was then found to be dissolved. The liquid, when it had become clear, was poured off, the residue again treated with sulphuric acid, &c.; and this treatment repeated till a residue was left on which the acid exerted no further action.

A. The acid solution was next subjected to the usual course of analysis, by means of hydrosulphuric acid, sulphide of ammonium, &c.

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* For the above determinations of the crystalline form and hardness of the mineral, I am indebted to Mr. Edward Chapman, of Kensington.

a. Hydrosulphuric acid threw down nothing but a trace of copper.

b. Sulphide of ammonium gave a copious black precipitate; and this, being dissolved in *aqua regia,* gave a yellow solution, in which ferrocyanide of potassium showed the presence of iron in small quantity. Ammonia, added in excess to this solution, produced a buff-coloured precipitate and a pinkish solution. This solution was found to contain a small quantity of cobalt. The buff-coloured precipitate was boiled in caustic potash; but nothing was dissolved. Fused with borax before the blow-pipe, it gave, in the outer flame, a glass, which was reddish-yellow while hot, but became colourless on cooling: in the inner flame, a perfectly colourless glass was produced. These characters might be due to the iron present. It was evident, however, that the precipitate contained something besides iron; and its insolubility, both in potash and ammonia, rendered the presence of earthy phosphates, borates, &c., probable. Boracic acid was, therefore, searched for in the usual way; but none was found. The presence of fluorine was impossible, since the mineral had been boiled in strong sulphuric acid. The mineral itself was likewise carefully examined for fluorine, but gave no indication of its presence. To search for phosphoric acid, it was necessary to separate the bases. For this purpose, I dissolved a portion of the buff-coloured precipitate in hydrochloric acid, and added oxalate of ammonia to the solution. This produced a copious precipitate; and I found that this same precipitate was produced even when the solution was very strongly acid, a large excess of acid merely rendering it necessary to add a greater quantity of the reagent. Oxalic acid acted in the same manner as oxalate of ammonia.

The precipitate thus obtained was of a very peculiar character. It was at first bulky and of a curdy consistence, like chloride of silver; but quickly became crystalline and sank down to the bottom of the vessel: it was nearly white, but had a perceptible tinge of violet. It was collected on a filter, washed and dried, and then ignited. It then underwent a remarkable change, becoming first black, then yellow, and acquiring an almost fluid consistence; the fine solid particles floating, as it were, in an atmosphere of the gases which were escaping.* Finally, the whole became tranquil, and assumed a dark brown-red or tile-red colour.

This brown-red substance, fused with borax before the blow-pipe, gave the characters already mentioned. Digested in hydrochloric acid, it remained unaltered in the cold; but on the application of a gentle heat, it dissolved with copious evolution of chlorine. The solution was yellow at first, but assumed a violet tint after longer boiling. It was then mixed with a tolerably strong solution of sulphate of potash, which, in a few minutes, threw down a copious white crystalline precipitate, insoluble in an excess of the reagent.

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* Translation of Gmelin's Chemistry, vol I. p. 212, note.

All these characters distinctly prove that the brown-red substance obtained as above, consists wholly, or in great part, of *Oxide of Cerium*. As, however, zirconia, yttria, and thorina, are likewise precipitated by oxalic acid from acid solutions, it was necessary to ascertain whether these substances were associated with the cerium or not. The solubility of the brown-red powder in hydrochloric acid proved the absence of zirconia; for that substance, after ignition, is insoluble in all acids, except concentrated sulphuric acid. Yttria is, like cerium, precipitated by sulphate of potash; but the precipitate is soluble in an excess of sulphate of potash. To ascertain, therefore, whether it was present, a saturated solution of cerium in hydrochloric acid was mixed with a saturated solution of sulphate of potash, and a crystalline crust of that salt introduced in such a manner, as to be in contact with the liquid throughout its whole depth. The whole was left to stand for several days, and then filtered. The filtrate mixed with excess of caustic potash gave no precipitate: therefore no yttria was present. The absence of thorina is proved in the same manner as that of zirconia; for thorina, after ignition, is insoluble in all acids except strong sulphuric acid.

The presence of *Lanthanum* and *Didymium*, the metals usually allied with cerium, was easily proved by methods hereafter to be described. It is interesting to find that these metals are associated with cerium in this hitherto unknown mineral, as well as in the Cerites, Orthites, &c., in which they have previously been discovered. It seems to show that the association of these three metals is not merely fortuitous, but exists in consequence of a regular law.

The acid liquid, from which the cerium, &c., had been separated by oxalate of ammonia, was next examined for phosphoric acid. For this purpose, a portion of it was tested with ammonia and sulphate of magnesia, which produced a copious crystalline precipitate, indicating the presence of phosphoric acid. To obtain additional proof of this, however, the remaining portion of the acid liquid was mixed with perchloride of iron and excess of ammonia. The precipitate was thoroughly washed to remove all traces of soluble chlorides, and then decomposed by digestion in sulphide of ammonium. The liquid filtered from the sulphide of iron thus produced, was boiled with nitric acid, and filtered again to free it from sulphur. The filtrate, treated with nitrate of silver and a small quantity of ammonia, gave the characteristic yellow precipitate of tribasic phosphate of silver. It appears, then, that the matter precipitated by sulphide of ammonium mainly consists of phosphate of cerium.

c. The liquid filtered from the black precipitate (*b*), produced by sulphide of ammonium was boiled with an excess of hydrochloric acid, and filtered to separate sulphur; the filtrate was evaporated to dryness, and ignited to expel ammoniacal salts. A trifling fixed residue was left, which appeared to be magnesia; but the quantity was too small to give distinct indications.

B. The matter insoluble in sulphuric acid was examined in the usual manner by fusion with carbonate of soda: it consists chiefly of silica, with small quantities of iron, alumina, and lime, and a trace of magnesia. It is merely sandy or argillaceous matter contained in the ore, and mechanically mixed with the crystalline powder.

The mineral appears then to consist essentially of *Phosphate of Cerium* (including lanthanum and didymium). The small quantity of cobalt found associated with it is merely accidental; its presence is easily accounted for when we remember the source of the mineral itself. The iron, which is in somewhat larger quantity, is probably contained in the substance of the crystals; its quantity, though not very great, is too large to be accounted for by the accidental presence of any magnetic particles which might have escaped the searching action of the magnet. I propose to call this substance PHOSPHO-CERITE.

QUANTITATIVE ANALYSIS.

A convenient quantity of the yellow crystals, separated as completely as possible from the magnetic particles, was reduced to a state of exceedingly minute division by pounding in an agate mortar, and subsequent levigation. The fine powder thus obtained having been thoroughly dried at a gentle heat, a quantity of it was weighed out, amounting to 51·46 grains. It lost nothing by strong ignition. It was dissolved as completely as possible in sulphuric acid, as in the quantitative analysis. The insoluble matter weighed 1·52 grains, or 2·96 per cent.

The cerium, &c., was precipitated by oxalate of ammonia, and the oxalate converted, by ignition, into sesquioxide of cerium associated with lanthanum and didymium. It weighed 35·76 grains. Now the atomic weight found by Berzelius and Hisinger for cerium—at a time when the existence of lanthanum and didymium was unknown, and that which is now known to be a mixture of the three metals, was regarded as a single metal—is, on the hydrogen scale, 46. Hence, the atomic weights of the protoxide and sesquioxide of cerium (using that term in its former sense) are to one another as 46 + 8 : 46 + 12, or as 54 : 58.

Now, 58 : 54 : : 35·76 : 33·29

Hence the quantity of protoxide of cerium, or rather of the protoxides of the three metals taken together, is 33·29 in 51·46 grains of the mineral, or 64·98 per cent. I have not attempted to determine the relative quantities of the three oxides. In the present state of our knowledge, indeed, this determination is impossible; partly, because the individual atomic weights of cerium, lanthanum, and didymium are unknown; partly because all the processes of separation hitherto devised are so tedious and complicated, and attended with so much unavoidable loss from the multitude of decantations, filtrations, and washings which they involve, that their application in quantitative analysis is quite out of the question.

The cerium, &c., having been separated as above, the filtered liquid was neutralized with ammonia, and sulphide of ammonium added. The precipitate was digested in nitric acid, and ammonia added in excess. The precipitate of peroxide of iron thus produced, weighed 1·50 grains, corresponding to 1·45 grains, or 2·83 per cent. of magnetic oxide, $Fe_3 O_4$, the state in which the iron most probably exists in the mineral. The ammoniacal solution, filtered from the iron precipitate, yielded a small quantity of oxide of cobalt, with a trace of copper, amounting to 0·23 gr. or 0·45 per cent.

Lastly, the filtered liquid containing the phosphoric acid was treated by Berthier's process for determining the quantity of that acid: the result was 14·65 grains, or 28·46 per cent.

We have then for the composition of the mineral, in 100 parts,

Protoxides of cerium, lanthanum, and didymium	64·68
Phosphoric acid	28·46
Oxide of iron ($Fe_3 O_4$)	2·83
Oxide of cobalt, &c.	0·45
Sand, &c.	2·96
	99·38

Or, disregarding the oxide of cobalt, and the matter insoluble in sulphuric acid, as adventitious, we find for the actual composition of the crystals:

Protoxides of cerium, lanthanum, and didymium	67·38
Phosphoric acid	29·66
Oxide of iron*	2·95
	100·00

Notwithstanding the apparent accuracy of the preceding analysis, it must not be considered as more than an approximation to the truth. For, the determination of the quantity of the associated bases rests upon the old atomic weight of cerium, found by Berzelius and Hisinger. Now, since that which was then regarded as a simple metal, is really a mixture of the three metals, whose several atomic weights are unknown, and as the proportions, in which the oxides of these metals are associated, is by no means constant, it is evident that the atomic weight of the compound metal must be liable to considerable variation; unless indeed the atomic weights of the individual metals are equal to each other, a coincidence which, though possible, we have no right to assume.† It must, however, be remarked that the same uncertainty rests upon the analyses of all minerals containing cerium in the state of protoxide, *e. g.* orthite, allanite, &c. If the number 46 be not the true expression of the atomic weight of the compound metal, *cerium*, all analyses of such minerals must be incorrect, inasmuch as the cerium can never be estimated *directly* in the state of protoxide. But since these analyses have all the appearance of accuracy, and have been made by chemists of unquestioned analytical skill (the greater number by Berzelius), it is scarcely probable that any very material error can have been committed in taking the number 46 as the atomic weight of cerium in the sense above-mentioned. The question must, however, remain undecided, till the three metals shall have been obtained in a state of purity, and their atomic weights individually determined.

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* It is, however, by no means certain that the iron exists in the crystals themselves. I took all possible pains to remove the ferruginous particles by the magnet; but it is very possible that a small quantity of iron may have been diffused through the crystalline powder in the form of *peroxide;* if so, the magnet would not have removed it.

† Berzelius states, on the authority of Mosander, that the atomic weight of lanthanum is greater than that of the combined metals, and nearly equal to 680 on the oxygen scale, or 54·4 on the hydrogen scale (*Traité de Chimie*, 5e. *Ed. Par.* t. II. p. 755). In a subsequent part of the same work (t. IV. p. 544), he says that the atomic weights of cerium, lanthanum, and didymium are unknown. In *Gmelin's Hand-book* (Translation I, 50), the atomic weight of lanthanum (or rather of lanthanum and didymium together) is said to be 36·1, and that of cerium 46·3. I mention these facts to show that the whole subject is beset with uncertainty, and still open to investigation.

While this uncertainty exists with regard to the combining numbers of the bases, we cannot, of course, arrive at any final conclusion respecting the atomic constitution of the mineral. If, however, we assume that the number 46 correctly expresses the atomic weight of the three metals considered as one (which may be denoted by the symbol M), and if we suppose that phospho-cerite is a tribasic phosphate of this metal, viz., $3\,MO, PO_5$, we shall have for its atomic weight,

$$3\,(46 + 8) + 71{\cdot}38 = 162 + 71{\cdot}38 = 233{\cdot}38;$$

and this reduced to 100 parts, gives

$$69{\cdot}41\ MO + 30{\cdot}59\ PO_5 = 100.$$

Now, if in the preceding analysis, we disregard the oxide of iron, which, even if it be contained in the substance of the crystals, is too small in quantity to be considered essential to their constitution—in other words, if we simply calculate the proportion of oxide of cerium, &c., and phosphoric acid existing in the crystals, we find as the result:

$$69{\cdot}44\ MO + 30{\cdot}56\ PO_5 = 100.$$

These quantities are almost identical with those above calculated from the formula $3\,MO, PO_5$, differing in fact by only 0·03 per cent. We cannot, perhaps, place very great reliance on this coincidence, on account of the uncertainty above alluded to; but it can scarcely be regarded as merely accidental. If the result be trustworthy, it will go far to prove that the atomic weight of the compound metal cannot differ greatly from 46.

If the view here taken be correct, it will follow that phospho-cerite is a mixture of the tribasic phosphates of cerium, lanthanum, and didymium. The isomorphism of these metals can scarcely be doubted; and it is, therefore, to be expected that their analogous compounds should crystallize together.

NOTE.—Since this paper was communicated to the Society, Mr. Chapman has kindly drawn my attention to the fact, that a mineral, nearly, if not quite, identical with phospho-cerite, was discovered and analysed by Wöhler about three years ago. It is thus described in the *Rapport Annuel* of Berzelius, 7e. année:

"Wöhler has found in the compact *apatite* of Arendal, a new mineral to which he has given the name of *Cryptolite* (κρυπτος). It occurs principally in the variety called *apatite rosé*, whence it is obtained in perfect crystals by dissolving the apatite in nitric acid, which leaves undissolved a number of small crystals of various minerals. Among these crystals occur those of cryptolite: they are a line in length, and are laid parallel to each other side by side. There also occur crystals of magnetic iron ore, amphibole, and a mineral of a hyacinth-red colour. The crystals of cryptolite may be separated by a pair of forceps. When examined by the microscope, they are found to be transparent, hexagonal prisms, of a wine-yellow colour. Their specific gravity is 4·6.

"Concentrated sulphuric acid decomposes them, the whole being reduced to a dry earthy mass. By analysis, they are found to contain:

Ceric oxide	73·70
Ferrous oxide	1·51
Phosphoric acid	27·37
	102·58

"The excess of this analysis is due to the oxygen of the ceric oxide, the mineral itself containing cerous oxide. The result of the analysis agrees sufficiently with the formula $\dot{\mathrm{C}}\mathrm{e}_3\,\overset{\cdot\cdot}{\overset{\cdots}{\mathrm{P}}}$ to justify the admission that the mineral is formed almost wholly of phosphate of ceric oxide.

"The hyacinth-red mineral likewise contained cerium; but the quantity of it was too small for analysis."

Such is Wöhler's account. The quantity of cerous oxide contained in the 73·70 of ceric oxide is 68·62; and the proportions of that oxide and phosphoric acid in 100 parts (leaving out the iron) are as 71·5 : 28·5. These quantities do not agree so closely with the formula $3\,MO, PO_5$, as those found in my own analysis; still there can be but little doubt that Wöhler's mineral is really a tribasic phosphate, and, therefore, identical in chemical composition with phospho-cerite. The specific gravities of the two minerals are likewise nearly the same. But the crystalline forms are totally incompatible; for the hexagonal prism can never occur as a modification of forms belonging to the square prismatic system; and as Wöhler's crystals were large enough to be picked out with the forceps, it is scarcely probable that he can have mistaken their crystalline form. For these reasons, I do not think it necessary to alter the name which I have given to the mineral obtained from the cobalt ore.

SEPARATION OF CERIUM, LANTHANUM, AND DIDYMIUM.

As the methods of obtaining these substances in a state of purity are not very generally known, and, as far as I am aware, are not fully described in any English work, I here subjoin a sketch of the several methods hitherto devised, adding such observations as my own experience has suggested. I shall first speak of the methods of separating cerium from lanthanum and didymium together, and afterwards of the separation of lanthanum and didymium from each other.

I. The separation of cerium from lanthanum and didymium depends upon this circumstance: that cerium forms two oxides, the protoxide or *cerous oxide,* and the sesquioxide or *ceric oxide;* the latter of which is nearly insoluble in weak acids; whereas lanthanum and didymium appear to be susceptible of only one degree of oxidation, and their oxides are easily soluble in dilute acids. On this principle is founded the first mode of separation devised by Mosander,* to whom we are indebted for the discovery of lanthanum and didymium.

This method consists in converting the mixed oxides of the three metals into chlorides, precipitating with a large excess of caustic potash, and subjecting the precipitate suspended in the liquid to the action of a stream of chlorine gas. The oxides of lanthanum and didymium then dissolve in the mixture of chloride of potassium, hypochlorite of potash, and excess of hypochlorous acid produced, while the cerium is peroxidized and remains undissolved. The precipitate first assumes a violet colour, then becomes yellow, and ultimately of a deep orange colour. When this has taken place, the liquid is found to be completely saturated with chlorine, and has acquired a yellow colour. The whole is then to be set aside for four and twenty hours in a close vessel, and afterwards the liquid separated by filtration from the insoluble ceric oxide, and treated with excess of caustic potash to precipitate the oxides of lanthanum and didymium. Such is the method by which Mosander first effected the separation of these oxides. He says that the ceric oxide, thus obtained, is quite free from lanthanum and didymium; but that the supernatant liquid, in addition to the oxides of those metals, likewise contains a small quantity of cerium, for the complete removal of which, the whole process must be repeated three or four times. In these respects, my own observations do not quite agree with those of Mosander. I find that the quantity of oxide of cerium dissolved in the chlorine liquid is very small, and is completely precipitated by boiling the solution till it loses its yellow colour: a salmon-coloured precipitate then separates, which is the oxide of cerium. If the boiling be then stopped, the liquid filtered, and the oxides of lanthanum and didymium precipitated by caustic potash, the precipitate thus obtained is quite free from cerium; for on being again subjected to the chlorine process, it dissolves completely without any deposition of oxide of cerium. On the other hand, I have always found that the ceric oxide, produced by the first application of the above process, retains considerable quantities of the other oxides, and that these can only be separated by repeating the process several times. I find it better, therefore, instead of leaving the liquid, after saturation, to stand in contact with the precipitate for several hours, to pour it off, fill up the vessel with fresh caustic potash, again pass chlorine through the liquid till it is saturated, and repeat this treatment till the yellow liquid, after being boiled till its colour disappears, and then filtered, no longer gives a precipitate with caustic potash. When this point is attained, the ceric oxide may be considered perfectly free from lanthanum and didymium. It retains, however, considerable quantities of hypochlorous acid and salts of potash. To free it from these, Mosander digests it at a gentle heat in a solution of potash, which removes the hypochlorous acid, and then dissolves out the potash by dilute nitric acid. The ceric oxide thus purified is then washed and ignited. I find, however, that a much more expeditious mode of purification is to dissolve the yellow ceric oxide in boiling hydrochloric acid, continuing the boiling till chlorine is no longer evolved, and then precipitate the cerium by oxalate of ammonia. The precipitate of oxalate of cerium thus formed is a heavy crystalline powder, which, when collected on a filter, may be washed with the greatest facility; and when subsequently dried and ignited, yields pure ceric oxide of a delicate cinnamon colour. This mode of separating cerium from the allied metals is long and tedious; but the result is certain and the separation complete.

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* Philosophical Magazine, vol. XXVIII. p. 241.

Another mode of separating cerium from lanthanum and didymium, also discovered by Mosander, is to digest the mixed oxides in very dilute nitric acid. The dark red-brown substance obtained by igniting a mixture of the oxalates, carbonates, or protoxides of the the three metals (for the sake of distinction I shall call it the *crude oxide* of cerium), consists of ceric oxide mixed with the oxides and carbonates of lanthanum and didymium. It dissolves readily in hot strong nitric acid. The solution, which is of a beautiful deep orange colour, and acquires, by concentration, the consistence of a thick syrup, leaves, when evaporated to dryness, a yellow gummy residue of nitrate of ceric oxide, together with the nitrates of the other two oxides. When this substance is ignited at a temperature sufficient to expel the nitric acid, it leaves a residue nearly, if not quite, identical with the crude oxide of cerium before treatment with nitric acid, but of a much lighter colour, and much less soluble in acids. These differences of colour and solubility appear to be nothing but a difference of aggregation. Now when this crude oxide of cerium, modified as above by treatment with nitric acid and subsequent ignition, is digested for several hours in very dilute nitric acid—about 1 part of acid in 100 parts of water, the lanthanum and didymium are dissolved, and the cerium left behind. One digestion in nitric acid is not, however, sufficient to remove the whole of the lanthanum and didymium. The liquid must be poured off after a while, and fresh acid supplied; and this process must be repeated till the acid liquid, after remaining for some time in contact with the ceric oxide, gives no precipitate with oxalate of ammonia. The ceric oxide is then left behind of a pure and beautiful cinnamon colour. This process appears, from description, to be much easier than that first described. It is, however, liable to certain inconveniencies. (1.) The oxide of cerium, when digested in the acid liquid, and more particularly if subsequently washed with water, becomes so minutely divided, that it diffuses itself through the liquid and will not separate for days; and if an attempt be made to filter the liquid, the solid matter first runs through the filter, and then completely stops it up. This inconvenience may be obviated to a considerable extent by warming the liquid, or rather by keeping it in a warm place during the whole time of digestion. But there is always a considerable difficulty in obtaining a clear solution, and in getting the ceric oxide completely free from the soluble matter. (2.) The separation is not always complete. The nitric acid generally dissolves a small quantity of cerium. To separate this, the acid solution must be evaporated to dryness, the residue ignited, and again digested in weak nitric acid: this process often requires to be repeated three or four times. When the ignited residue dissolves completely in cold dilute nitric acid, the oxides contained in the solution may be precipitated by caustic potash, or the solution evaporated to dryness, and the residue ignited to expel nitric acid. To make quite sure of the absence of cerium, a small portion should be tested by the chlorine process above described: if any cerium should still be found remaining, it is best to treat the whole by that process. When the oxide of cerium has been freed as much as possible from lanthanum and didymium, a small portion of it should be boiled in strong hydrochloric acid. If pure, scarcely a trace will dissolve, with a barely perceptible evolution of chlorine. A solution may, however, be obtained by the aid of alcohol, which deoxidizes the ceric oxide, and reduces it to a state of cerous oxide: the acid then dissolves it. The solution thus obtained should be tried by the chlorine process to ascertain if any didymium be left behind. If so, the ceric oxide may be digested for a while in moderately dilute hydrochloric acid, which will dissolve the remainder of the didymium. The nitric acid is sure to remove the whole of the lanthanum. It is remarkable that the ceric oxide, obtained by this process is always of a lighter colour than that obtained by the process first described. Even if it be dissolved in acid, precipitated as an oxalate, and the oxalate again converted into ceric oxide by ignition, the light colour is retained. I was at first inclined to attribute this difference to the greater purity of the ceric oxide obtained by the latter process: but I have carefully tested that obtained by the chlorine process, by digesting it for a long time in hydrochloric acid, and have not been able to discover a trace of didymium in it. I attribute the difference of colour merely to a difference of aggregation: I have already observed that the crude oxide of cerium acquires a lighter colour by mere solution in nitric acid, evaporation to dryness, and ignition. A modification of the preceding process has been suggested by Berzelius. I shall notice it in speaking of the separation of lanthanum and didymium.

A method of separating cerium from didymium by means of valerianic acid has been devised by L. L. Buonaparte.* It is thus described by Berzelius.† "The hydrated oxides are precipitated by a caustic alkali, and the cerous oxide converted into ceric oxide. The whole is then dissolved in nitric acid—the excess of acid driven off by evaporation at a gentle heat—the residue mixed with a very small quantity of water, and a saturated solution of valerianic acid added drop by drop as long as any precipitate forms. This precipitate is the valerianate of ceric oxide; valerianate of didymium remains in solution." It is not stated whether this reagent will separate lanthanum from either of the other oxides: but there is every probability that its action on lanthanum will be the same as on didymium. I have not tried the method, as I do not think that it can ever be made available, excepting on a very small scale, on account of the great trouble of preparing the acid. Besides, we have easier methods of separating cerium from the other two metals.

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* Comptes rendus, t. XVI, p. 1008.

† Traité, II, 752.

II. *Separation of Lanthanum and Didymium.*—A solution of these substances, free from cerium, having been obtained by either of the preceding processes, they may be precipitated, either as hydrated oxides by means of caustic potash, or, as oxalates by the addition of oxalate of ammonia. I prefer the latter method, because the filtration and washing are so much more expeditious than with the former. The oxalates are then to be converted into carbonates by ignition, and the carbonates dissolved in dilute sulphuric acid. The separation of the two metals depends upon the different degrees of solubility of their sulphates; and the mode of effecting it is different, according as the lanthanum or the didymium is in greater quantity. This may be known by the colour of the solution. When the didymium is in excess, the solution has a decided pink colour, even when dilute; but when the quantity of that metal is but small, the liquid is colourless when dilute, and does not assume a pink colour till highly concentrated.

When the lanthanum is in excess, Mosander recommends the following process. The solution containing the mixed sulphates is to be evaporated to dryness, and the residue ignited to expel the water of crystallization, and the excess of sulphuric acid. The anhydrous sulphates are then to be dissolved in rather less than six times their weight of water, at a temperature of 36^0 or 37^0 Fah., the powder being added by small portions at a time, and the vessel containing the liquid being surrounded by ice-cold water, to prevent the rise of temperature consequent on the combination of the anhydrous sulphates with water. If this precaution be not taken, and the temperature of the liquid consequently rise above 48^0 Fah., crystallization commences and rapidly extends throughout the whole mass of liquid. If, however, the water be properly cooled, the anhydrous sulphates dissolve completely. A solution having been thus obtained, it is to be gradually raised by a water-bath to a temperature of rather more than 103^0 Fah., when the sulphate of lanthanum will crystallize out, contaminated however with sulphate of didymium, which gives it a rose colour. To purify it completely from didymium, Mosander directs that it be again rendered anhydrous, redissolved in ice-cold water, &c., the whole process requiring to be repeated ten or twelve times before the sulphate of lanthanum is obtained perfectly pure. I have made three or four trials of this process with all possible care, but have never succeeded in getting the sulphate of lanthanum to crystallize out in the manner above described. Probably the substance on which I have operated is richer in didymium than those on which Mosander's experiments were made. At all events, the process, as may be seen from the preceding description, is excessively long and troublesome; and I believe that a pure salt of lanthanum may, in all cases, be more readily obtained by that which I am about to describe.

The sulphates of lanthanum and didymium have this remarkable relation, that though the sulphate of lanthanum is less soluble than the sulphate of didymium in a neutral solution, yet from an acid solution, the sulphate of didymium crystallizes out first. Accordingly, a pure salt of didymium is easily obtained as follows. A solution of the mixed sulphates containing excess of sulphate of didymium is strongly acidulated with sulphuric acid, and left for two or three days in a warm place. Two sorts of crystals then collect at the bottom of the basin: 1. Large rose-coloured rhombohedral crystals, modified with numerous secondary faces. 2. Slender prismatic violet-coloured crystals which adhere to the sides of the vessels. The latter consist of the two sulphates mixed; the former are sulphate of didymium: these are to be selected from the rest, separated as much as possible from adhering sulphate of lanthanum, by rapidly washing them with hot water, and finally purified by recrystallization. This is also Mosander's process. I have invariably found it successful. But further—I find that by redissolving the prismatic violet crystals above spoken of—mixing the solution with the mother-liquid, and again subjecting it to slow evaporation, though no more large crystals of didymium-salt are obtained, the liquid yields rhombohedral crystals of a violet colour; and by taking these out, evaporating the mother-liquor still further, and repeating these operations three or four times, the solution at length becomes perfectly colourless, and when evaporated to dryness, yields a colourless residue of sulphate of lanthanum. The solution in this state likewise yields perfectly colourless precipitates with alkalis and alkaline carbonates, and also with oxalic acid. This is the only method by which I have yet succeeded in obtaining a pure salt of lanthanum. It is sufficiently tedious, but the result is satisfactory.

I have already spoken of a process suggested by Berzelius* for separating lanthanum and didymium: it is as follows. The crude oxide of cerium, after solution in nitric acid and subsequent ignition, is digested for a while in very dilute nitric acid (1 part of acid in 100 of water), the solution is then poured off, and the residue digested in dilute hydrochloric acid. The nitric acid removes nearly all the lanthanum, together with small quantities of didymium and cerium, and the hydrochloric acid dissolves out all, or nearly all, the didymium, together with the remaining portion of lanthanum, and more or less of cerium. The cerium may be removed from both solutions by evaporating to dryness and redigesting in dilute acid, repeating the process till no insoluble residue remains—or else by the chlorine process. The nitric acid solution always contains more or less didymium, sometimes a considerable quantity: the longer the digestion is continued, the greater is the quantity of didymium dissolved. It may, however, be completely removed by converting the salts into sulphates and crystallizing out the sulphate of didymium from an acid solution. From the hydrochloric acid solution, a pure salt of didymium may readily be obtained by precipitating with caustic potash, dissolving the precipitate in excess of sulphuric acid, and crystallizing by spontaneous evaporation as above described. The ceric oxide also, after digestion in hydrochloric acid, is almost sure to be pure. On the whole, this process affords a ready means of obtaining salts of lanthanum and didymium nearly pure: if absolute purity be desired, they must be farther treated by the methods above indicated.

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* Traité de Chimie, 5e., Ed. II. 752.

The salts of lanthanum and didymium are distinguished from one another by marked characters. All the salts of didymium are coloured, some being pink or rose-coloured, and others violet. The sulphate is rose-coloured, so also is the nitrate: the solution of the nitrate, however, when highly concentrated, is violet-blue by reflected light. The hydrated oxide and the carbonates are violet; so likewise is the oxalate. When either the oxalate, the carbonate, or the hydrated oxide is ignited, it yields the anhydrous oxide, which is of a dark brown colour. It is this oxide which gives the dark red-brown tint to the crude oxide of cerium; it is readily soluble in dilute acids; when exposed to the air, it absorbs carbonic acid.

All the salts of lanthanum are white. The oxalate, when ignited, first turns black from the separation of carbon; and when this is burnt away, perfectly white carbonate of lanthanum is left. This, when more strongly ignited,—especially in an open vessel—is converted into a light brown substance, which is the anhydrous oxide. In Mosander's memoir, this oxide is said to be nearly white; and the slight brown colour which it has is attributed to the presence of a minute quantity of didymium. This, however, I cannot but regard as doubtful; for I can perceive no difference of colour between the anhydrous oxide obtained by igniting perfectly white carbonate of lanthanum, and that produced from carbonate which I know to be slightly contaminated with didymium. When carbonate of lanthanum in small lumps is ignited, the surface of the lumps turns brown, while the inner portions remain perfectly white; when carbonate of didymium is similarly treated, the whole becomes dark brown in a very short time. Anhydrous oxide of lanthanum attracts carbonic acid from the air more rapidly than oxide of didymium: the hydrated oxide, which is perfectly white, absorbs carbonic acid so rapidly that, when washed on a filter, it is wholly converted into carbonate before the washing is complete.

It will be seen, from the preceding observations, that the main difficulty in all these processes is to obtain a pure salt of lanthanum. It is difficult even to ascertain when that result is attained; the only test is the perfect whiteness of the salts: the least trace of didymium imparts a violet colour to a concentrated solution, which a practised eye can readily detect. I was for a long time led away by the expectation of obtaining anhydrous oxide of lanthanum perfectly white: and have spent a great deal of time and labour in endeavouring to get rid of a colour which, I am now inclined to believe, is essential to the substance.

Since writing the above, I have found that the oxides of lanthanum and didymium may be completely separated from oxide of cerium by boiling the crude oxide in solution of sal-ammoniac, after having dissolved the oxide in nitric acid, and driven off the acid by ignition, as already described. The ceric oxide thus obtained is of a delicate fawn colour. I have not yet been able to examine the results minutely: but the portions first dissolved appear to contain but a very small quantity of didymium. This being the case, it is probable that, by using a weak solution of sal-ammoniac, and properly fractioning the products, a pure salt of lanthanum may be at once obtained. At all events, this process, as far as I have examined it, seems more likely to yield good results than any that I have previously tried. I shall pursue this investigation, and hope soon to have more definite results to lay before the Society.

XV.—*On Isomorphism, &c., and on a simple law, governing all crystalline forms, by* H. B. LEESON, M.D.

MY former papers were more especially intended to conduce to a correct reading of crystalline forms, and to show the relationship which all crystals possess to certain lines of direction, termed gubernatorial axes, such axes not being arbitrarily chosen, but coinciding with the directions of the aggregating forces, magnetic and electric, and evidenced by the state of tension existing in the interior of the crystals, as exhibited when such crystals are examined by polarized light.

I am the more anxious to impress upon all those advancing doctrines, having reference to crystalline form, the necessity of a correct understanding of the crystals on which their observations are based, because, I observe in numerous papers on Isomorphism, Dimorphism, &c., that forms have been considered primary, although only secondary modifications; and that substances have been ranked as dimorphous, although, in fact, only crystallized in different varieties of the same system or class.

If Isomorphism, as the name would imply, had reference, simply, to the same external configuration, then all substances would be polymorphous; for although, only one form may have hitherto been observed in any particular substance, still the instances are so numerous in which the same substance (as for instance: fluor spar sulphate of barytes, or, carbonate of lime,) does crystallize, in a variety of forms, that, judging from analogy, we have reason to believe, every substance may be similarly varied; or, to convey our meaning in other words; that each substance may crystallize in uniaxial biaxial, and triaxial forms, such forms being still further varied by imperfect or defective development, elongation and composition, for the understanding of which, I must refer to my former papers, as printed in the Memoirs of the Chemical Society.

The term, isomorphous, is now, then, generally employed with reference only to the *system* in which a substance is supposed to crystallize; and such system or class must be determined by the position and length of the gubernatorial axes. Perhaps I may be excused for suggesting, that the term, *omo-axed*, or *simil-axed*, would better convey the idea intended, and prevent that misconception which evidently exists in the minds of some observers.

Since I first noticed the *similarity of the series* of forms, *occurring in each class*, I have been enabled, very considerably, to enlarge my collection, by specimens exhibiting a regular gradation of such forms. This has enabled me to apply the goniometer, formerly described to the measurement of the inclination of *edges*—as well as of planes, in a very extensive series of crystals. Thus it is that I have been led to observe a very simple relation, indicating the law, by which so far as my own observations extend, every variety of crystalline form seems to be engendered.*

Premising that the law itself is masked (as explained in my former papers) by the unequal development of particular planes; that such unequal development sometimes occasions the defect of certain planes, and that by elongation or combination of separate forms, the external aspect of a crystal may be still further complicated, I proceed to enunciate the principle, according to which, as I believe, all perfect forms are produced. Of course in examining a particular crystal, those planes must be selected, which belong to the same simple form, then, such form must be considered, as it would exist, if all the planes were equally developed, and any defective planes supplied, all this will be the more readily accomplished, when the method of Nature's proceeding, and the series of forms, is fully understood.

To enunciate then, the principle. *The perfect simple forms constitute a series, commencing; First, with the uniaxial form, and subsequently composed of six pyramids of four or eight sides, placed one at each extremity of the three gubernatorial axes. Such pyramids succeeding each other by a similar, and regular gradation,* WHATEVER BE THE SYSTEM *or disposition, and normal length of the gubernatorial axes.*

The series then may be considered as composed:

FIRST, of the uniaxial form. A six-sided parallelopiped, described in my former papers as produced by a plane, placed on each extremity of the gubernatorial axes, so as to be parallel to the other two axes. The planes of this form may be considered as the lower limit, or zero in height of the biaxial† pyramids.

SECONDLY, *of alternate triaxial and biaxial forms,* consisting each, of six four-sided pyramids, replacing, or surmounting, as it were, the uniaxial planes; and placed on each extremity of the gubernatorial axes, in such a manner, as that a line joining the apices of the opposite pyramids, corresponds to the gubernatorial axis; whilst the four sides of each pyramid are parallel, in the biaxial forms, to the four edges of the uniaxial plane they respectively surmount; and, in the triaxial forms, to the diagonals of such plane.

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* In my former papers, I have already shewn, that uniformity in the measurement of the inclination of planes, is far from constant, and that the mathematical accuracy, supposed to be attainable, is not to be expected. My own goniometer and the microscope, have still further convinced me, that planes, apparently perfect and brilliant to the naked eye, are full of inequalities; and, I believe, that in fluor, want of attention thereto, and of microscopic examination, has caused inclinations to be taken for planes, which really consisted of step-like diminutions, whilst in that substance, as in bismuth and other metals, forms have been considered rhombic, resulting merely from the unequal deposition, or subsequent removal (by solution, or otherwise) of lamina, on one or more edges of the crystal.

† By referring to my preceding papers, it will be understood that the term "biaxial" means that the planes cut two of the gubernatorial axes, and are parallel to the third axis, whilst "triaxial" planes cut all three axes.

These forms succeed each other in a series, produced by a continual replacement of the four lateral edges of the pyramid by planes; so that each succeeding or preceding pyramid differs, or revolves, as it were, 45° on the uniaxial plane.

And, THIRDLY, of a series of triaxial forms, composed of six eight-sided pyramids, produced as it were by a duplicature or repetition of the pyramids of the triaxial forms in the preceding or second series. Each eight-sided pyramid consisting of planes joining the four lateral edges of a pyramid of one of the triaxial forms in the preceding series, with the four lateral edges of another equal and similar pyramid, placed in the reverse or biaxial direction, so that the bases of the two pyramids, thus joined together, differ from each other 45°.

The primary triaxial form, may be considered as the first pyramid of the series, or point of departure; from which, by the continual replacement of edges, by planes, the most usual and *descending* series of pyramids, of lower height, is produced; whilst, by replacement of planes by edges, an *ascending* series of more acute pyramids may be obtained. The *ascending* series will necessarily consist of only two pyramids, joined base to base, otherwise re-entering angles, as subsequently explained, would be produced, which is inconsistent with a perfect form.

As an illustration of the principle, I will describe the series as occurring in the regular, or as I term it, the rectangular equiaxial system, as that in which the succession may be most easily comprehended; but I hope it will be fully understood, that the *same series exists in each of the other systems* and that I *possess* numerous specimens to substantiate such position, particularly in the oolique, and right oblique classes; figures of which, I am preparing for publication, in which the planes, belonging to each member of the series, will be designated by a particular colour, so as to exhibit, at one glance, the various perfect forms entering into the composition of any particular crystal.

To describe then the series as occurring in the regular system. The figures referred to being those given with my former papers.

FIRST.—*Primary uniaxial* form, Cube, Fig. 7, Pl. VII.

SECOND.—*Primary triaxial* form, Octahedron, Fig. 7, consisting of six four-sided pyramids, placed diagonally on the faces of the cube, so as to bisect the four edges of each face. The height of the pyramid being such that the planes of the three pyramids, surrounding each corner of the cube, coincide in one plane; thus each plane of the octahedron may be considered as composed of the planes of three separate pyramids, and corresponds to the lower limit or zero of the three-sided pyramid to be observed in each succeeding triaxial form: the solid angles of the cube being the upper limit or zero of height of the three-sided pyramid.

Third.—*Primary biaxial* form, Rhomboidal dodecahedron, Fig. 8. By replacing the twelve edges of the octahedron by planes, the rhomboidal dodecahedron is produced, and it will be readily observed in Fig 8 that it consists of six four-sided pyramids placed with their sides parallel to the edges of the cube, the height of the pyramid being such, that the planes of the two pyramids adjacent to the same edge coincide, and thus form one plane. If the pyramid were of lower height, as in the succeeding biaxial forms, the planes would as it were double over the edge, and thus give rise to twenty-four instead of twelve planes. If the pyramid were of greater height, the angle across the edge would be a re-entering angle. Hence this form is the limit of the height of the pyramid in the biaxial forms.

FOURTH.—*Second triaxial* form, Trapezohedron, Fig. 21, Pl. X. This form results from a replacement of the edges of the rhomboidal dodecahedron by planes, and may be easily observed to consist of six four-sided pyramids, the sides of which are parallel to the diagonals of the sides of the cube; but in consequence of the manner in which the planes necessarily intersect each other at their bases, the planes themselves lose their triangular outline, becoming in fact trapezoidal, and thus obscuring the pyramidal nature of the form. The height of the pyramid being less than in the primary triaxial form, originates a three-sided pyramid, corresponding to each face of the octahedron, and the form might thus be considered as composed of eight three-sided pyramids. The solid angles of the cube or uniaxial form being the upper limit or zero in height of these three-sided pyramids. A line joining the opposite pyramids corresponds, of course, to a diagonal of the uniaxial form.

FIFTH.—*Second biaxial* form, Pyramidal hexahedron, Fig. 7, Pl. X., produced by planes replacing the edges of the last form, and evidently consisting of six four-sided pyramids of lower height than those of the primary biaxial form, and, therefore, doubling over the edges of the uniaxial form, as already explained. This doubling originates a six-sided pyramid, corresponding to each face of the octahedron or primary triaxial form. Hence the diagonals of the uniaxial form join the apices of the opposite six-sided pyramids.

SIXTH.—*Third Triaxial* form, a more obtuse trapezohedron.

SEVENTH.—*Third biaxial* form, a more obtuse pyramidal hexahedron.

EIGHTH.—*Fourth triaxial* form, a trapezohedron still more obtuse.

NINTH.—*Fifth biaxial* form, a pyramidal hexahedron, with still flatter pyramids.

Unless in fluor, what I consider as step like striæ be considered planes, I have no specimens carrying this second series beyond the fifth biaxial form.

THIRD SERIES.—*First*, a duplicature of the primary triaxial form or octahedron. The Triaxisoctahedron, Fig. 24, Pl. VIII., formed of planes, joining the edges of the primary triaxial form or octahedron with those of another equal and similar octahedron resolved 45°, thus forming a figure compounded of six eight-sided pyramids, placed on the extremities of the gubernatorial axes, or of eight three-sided pyramids placed on the faces of the octahedron. The line joining the apices of the opposite three-sided pyramids corresponds to the diagonals of the uniaxial form. These three-sided pyramids are, it will be observed, in reverse position to those belonging to the trapezohedron. Compare Fig. 24, Pl. VIII. with Fig. 7, Pl. VII.

Second form, a duplicature of the second triaxial form or trapezohedron, producing the Tetraconta Octahedron, Fig. 21, Pl. VIII., composed of 48 planes, joining the four lateral edges of the six pyramids of the second triaxial form, with the four lateral edges of six other equal and similar pyramids placed in the reverse or biaxial direction, each plane of the cube or primary uniaxial form is thus surmounted or replaced by an eight-sided pyramid, and each solid angle of the cube or face of the octahedron by a six-sided pyramid.

Third form, a Tetracontahedron, derived from a duplicature of the third triaxial form, and hence more obtuse.

Fourth, a still more obtuse Tetracontahedron, derived from the fourth triaxial form.

Beyond this point, I do not possess, nor have I met with any specimen.

Thus, it is evident, that if one number of the series can be fairly made out, all the others may be deduced from it; and I have greatly assisted my labours by preparing and keeping by me a table of the successive angles of inclination, assuming 78°, 20′ as the most frequently occurring acute angle of the oblique uniaxial forms.

In conclusion, I would refer to a few circumstances which have tended, as I believe, to erroneous conclusions.

First, too much reliance on the perfection of planes, which on examination by the microscope, would have been found imperfect.

Next, assigning a primary position to planes of a secondary character. I have already sufficiently indicated, in my former paper many instances of this description.

I have, in my collection, perfect rhomboids of fluor spar, produced by the defect of two planes of the octahedron, as indicated in Fig. 23, plate XII.; and yet no one has hitherto ventured to pronounce fluor dimorphous. Again, I have cubes of fluor apparently rhombic, from the unequal deposition of laminæ, before referred to, and yet similar discrepancies in bismuth and antimony have induced some to consider such crystals as not belonging to the regular system.

But again, since by defect of planes, consequent on the undue development of the planes of any two opposite four-sided pyramids, every form may become octahedral. It is evident, that the apparent proportional length of the axes in different supposed octahedra of the same substance may be greatly varied, and thus a substance, actually belonging to the regular system, may be referred to the pyramidal, merely in consequence of the octahedron examined, not being the primary triaxial variety, but a portion of another form. I have crystals, both of copper and of silver, illustrating this position; and which, if they had occurred to other observers, would, I have no doubt, have induced them to class these substances, as like tin similarly circumstanced, dimorphous. Cleavage, in such cases, would evidently afford no assistance; and here again I may observe, too much reliance must not be placed on the coincidence of cleavage planes with those of the uniaxial form. In fluor it is well known the cleavage planes correspond with the primary triaxial planes; and, I believe, that in the right oblique system they frequently coincide with the primary biaxial planes.

Lastly, I would caution persons not to consider crystals as pseudomorphous, merely because they are of unusual occurrence amongst the specimens of the substance. If there is no reason to suppose the crystals have been actually moulded in the matrix of some other crystal, the term is not appropriate. I have primary uniaxial and triaxial specimens of quartz, which others would term pseudomorphous, but which, I believe, have not been formed in any matrix, and are only so termed, because persons have not been accustomed to believe in the existence of such forms.

March 19, 1849.

The President, in the Chair.

The following presents were announced:

"Memoirs upon Natural History," collected by W. Haidinger, and published by subscription, and "Reports upon the Communications of the Friends of Natural Science in Vienna," from W. Haidinger.

Messrs. C. F. Birnaud, G. Simpson, E. Packard and R. Prosser, were elected members of the Society.

The following papers were read:

Analysis of Berlin Porcelain, by MR. WILLIAM WILSON, *Student in the Royal College of Chemistry.*—The specimen analysed was taken from an evaporating dish and the quantities of the different ingredients were estimated by the usual analytical processes. The specimen as shown by the composition detailed below, was richer in silica and protoxide of iron than is usually the case, while there is a deficiency in alumina and potash.

Silicic acid	71·34
Alumina	23·763
Protoxide of iron	1·743
Lime	0·5686
Magnesia	0·1923
Potash	2·001

XVI.—*Note on the Phospho-cerite of Mr. Watts.*

BY EDWARD J. CHAPMAN, ESQ.

The object of this communication is to point out the apparent identity existing between the *Phospho-cerite*, so ably analysed by Mr. Watts, and a mineral discovered by Wöhler about three years ago, and named by him *Cryptolite*, from the Greek word κρυπτος, *concealed.*

This substance is contained, with several other minerals, in the rose-coloured apatite of Arendal, in Norway, and is obtained, according to Wöhler, in very minute hexagonal crystals, of a wine-yellow colour, by dissolving the apatite in nitric acid. It is associated with microscopic crystals of magnetic-iron-ore, hornblende, and an unknown substance, of a hyacinth-red colour, containing cerium.

The specific gravity of the cryptolite was found to equal 4·6, and its analysis furnished:

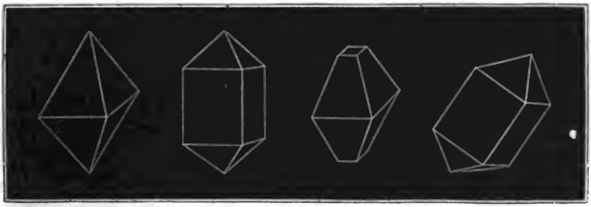
Phosphoric acid	27·37
Peroxide of cerium	73·70
Protoxide of iron	1·51
Total	102·58

The excess arises from the protoxide of cerium, contained in the mineral, being converted by ignition into peroxide. If we calculate these results after the atomic weight of the mixed metals, cerium, lanthanum and didymium, the cryptolite may be considered a tribasic phosphate of the protoxide of cerium ($3\ CeO, PO^5$), and, as such, identical in composition with the phospho-cerite of Mr. Watts, allowing the cerium of Wöhler's analysis to be a mixture of the three metals.

Having stated to Mr. Watts my intention of offering a few remarks on the existing phosphates of these bases in reference to his phospho-cerite, that gentleman kindly presented me with a small quantity of the mineral for examination. It occurs, when separated from the Dannemora cobalt by nitric acid, in the form of a fine powder, consisting of crystalline grains, partly of a pale sulphur-yellow colour, and partly colourless; possessing a degree of hardness equal to 5·0 5.5, and exhibiting in an eminent degree, when examined by the microscope, a peculiar vitreo-resinous or adamantine lustre. The specific gravity, as determined by Mr. Watts, is 4·78.

The greater number of the grains have no definite form, their edges appearing more or less rounded; but here and there may be recognised, although by no means distinctly, certain crystals, of which, after a careful investigation, I have been able to make out the three following forms: first, a more or less acute octahedron, fig. 1; secondly, a combination of that form with a four-sided prism, fig. 2; and thirdly, an octahedron with its apices replaced by apparently a single plane, fig. 3. Figures 2 and 3 shew that the octahedron is not a regular one, as all the edges in the one case, and the angles in the other, are not modified simultaneously; and from the general character of the crystals, I have been led to attribute them to the dimetric or square prismatic system. It must be confessed, however, that they do not present any visible modifications by which this deter-

FIG. 1. FIG. 2. FIG. 3. FIG. 4.



mination can be rendered certain, and from their extreme minuteness, it is of course impossible to ascertain by measurement whether the prism be a right one or not. These forms, therefore, do not exclude the mineral from either the trimetric or monoclinic systems (prismatic and oblique-prismatic systems of Möhs), but they show incontestibly that it cannot belong to the hexagonal or rhombohedral group, as the prisms of that system of crystallization cannot possess four lateral planes.

In this lies the principal difference between the phospho-cerite and Wöhler's cryptolite. If the crystalline form of the latter belong to the hexagonal system, the tribasic phosphate of protoxide of cerium must be dimorphous; but, on the contrary, if it belong to the trimetric or monoclinic systems, the hexagonal crystals of Wöhler are easily accounted for, by the truncation of either the obtuse or acute lateral edges of the primary, giving rise to the two planes h^1 or g^1 (in the nomenclature of Levy and Dufrénoy), and thus forming a six-sided prism. I should here state, also, that on my first examination of the minute grains of the phospho-cerite, I fancied that I detected hexagonal prisms amongst them; but I found afterwards, that this proceeded from my having obtained a strong outline in relief of the little prismatic crystals, as they rested upon one of their lateral planes. If we take the outline of figure 2, for instance, it will present an hexagonal form, appearing thus, when viewed by transmitted light, like the base of a six-sided prism. See fig. 4.

If the phospho-cerite really belong to the dimetric system, it may be considered isomorphous with the tribasic phosphate of Yttria, the phosphyttrite of Berzelius; and I may mention, as a curious coincidence, that this latter mineral has lately been found associated like the phospho-cerite, with some of the Swedish cobalt ores.

Allowing the phospho-cerite and the cryptolite to be identical, the mineral kingdom would appear to possess two distinct phosphates of cerium, one of the protoxide, and one of the peroxide, the monazite or mengite of Mr. Brooke; this latter mineral causing the evolution of chlorine, when decomposed by hydrochloric acid. Considering, however, the fact, that the amount of phosphoric acid in these minerals, from four different analyses, by Mr. Watts, Wöhler, Erdmann, and Hermann, does not exhibit a difference of 1 per cent, and that the protoxide of cerium is very readily converted, by atmospheric causes even, into the peroxide, might we not be tempted to regard the monazite as an altered phospho-cerite, and to look upon the red grains, found by Wöhler with the cryptolite, as forming a transition from one to the other. The monazite, it is true, crystallizes in the monoclinic or oblique-prismatic system, but this, I have shewn, is not incompatible with the forms assumed by the phospho-cerite, and the more so, as the angle *M, M* of the monazite, 92° 30′, closely approaches a right angle.

Exposed to the blow-pipe, the phospho-cerite vitrifies partially on the edges and surface, tinging the flame at the same time slightly green. With the usual blow-pipe re-agents, it presents the reactions of cerium, imparting, however, to the borax and phosphate of soda glasses, when cold, a pale violet-blue tint, either due to the presence of didymium, or to an admixture of a minute portion of the cobalt ore. With boracic acid and soft iron-wire, it produces a brittle globule of phosphuret of iron.

XVII.—*Researches on the Electrolysis of Organic Compounds.*

BY DR. H. KOLBE.

COMMUNICATED BY DR. A. W. HOFMANN.

The following investigation has chiefly arisen from some former observations[*] respecting the transformations of chloro-carbo-hyposulphuric acid, hydrochloric acid, and several other substances under the influence of oxygen, when liberated in the circuit of the galvanic current.[†] The facility with which, particularly the former acid, resisting in the moist way the most powerful oxidizing processes, is decomposed under these circumstances, appears to point to electrolysed oxygen as one of the most valuable oxidizing agents which are at the disposal of the chemist. Its application in chemical decompositions acquires additional importance, since its intensity may be varied, either by concentrating and heating the liquid, or by increasing or diminishing the number of elements producing the electrical current.

Starting from the hypothesis that acetic acid is a conjugated compound of oxalic acid and the conjunct methyl, I considered it, under these circumstances, not at all improbable that electrolysis might effect a separation of its conjugated constituents, and that, in consequence of a simultaneous decomposition of water, carbonic acid, as a product of the oxidation of oxalic acid, might appear at the positive, while methyl, in combination with hydrogen, viz., as marsh-gas, would be observed at the negative pole.

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[*] Observations on the oxydizing action of oxygen when disengaged by means of voltaic electricity in the "Memoirs and Proceedings of the Chemical Society," vol. III. p. 285.

[†] In the above cited investigation it was intended to state, that in the oxidation of hydrochloric acid by means of the electrical current, chloric acid appears at the positive pole even without the presence of an alkali. The sense of the sentence has been seriously altered by a misprint on page 287, line 8 from the top, *hypochloric* having been substituted for "hydrochloric acid." The sentence should have been as follows: "I have ascertained that when a voltaic current is passed through hydrochloric, and especially when previously mixed with some sulphuric acid, free chloric and perchloric acids are formed after the disengagement of a considerable quantity of chlorine."

The decomposition, which actually takes place, is not in perfect accordance with this supposition, as will be seen by the experiments hereafter described. The results obtained, however, are by no means less interesting, and deserve particular attention, opening as they do a prospect that the electrolytical decomposition of organic compounds will afford most important disclosures with reference to their chemical constitution.

After having made some preliminary experiments with several acids belonging to the acetic acid series, the products of the oxidation of valerianic acid appeared particularly suited for minutely following out the course of this decomposition. I therefore consider it convenient, first to describe the phenomena attending the decomposition of this acid, inasmuch as they form the basis for further experiments.

ELECTROLYSIS OF VALERIANIC ACID.

Valerianic acid being, like acetic acid, a bad conductor of electricity, I employed in the electrolytical decomposition a concentrated solution of its potash salt, prepared by neutralizing carbonate of potash, free from chloride, with pure valerianic acid, distilling at 175° (347° F.)*

The decomposing apparatus, *Fig.* 1,† is a glass cylinder, 11 inches in height and 2½ inches in diameter, which may be closed by means of a cork; in this is fastened a cylinder of sheet copper, closely approaching the sides of the glass, and to which is soldered the copper wire *a*, slightly projecting from the vessel. Within the copper sheet is another cylinder of platinum foil of somewhat smaller diameter, terminating in the platinum wire *b*, and prevented contact with

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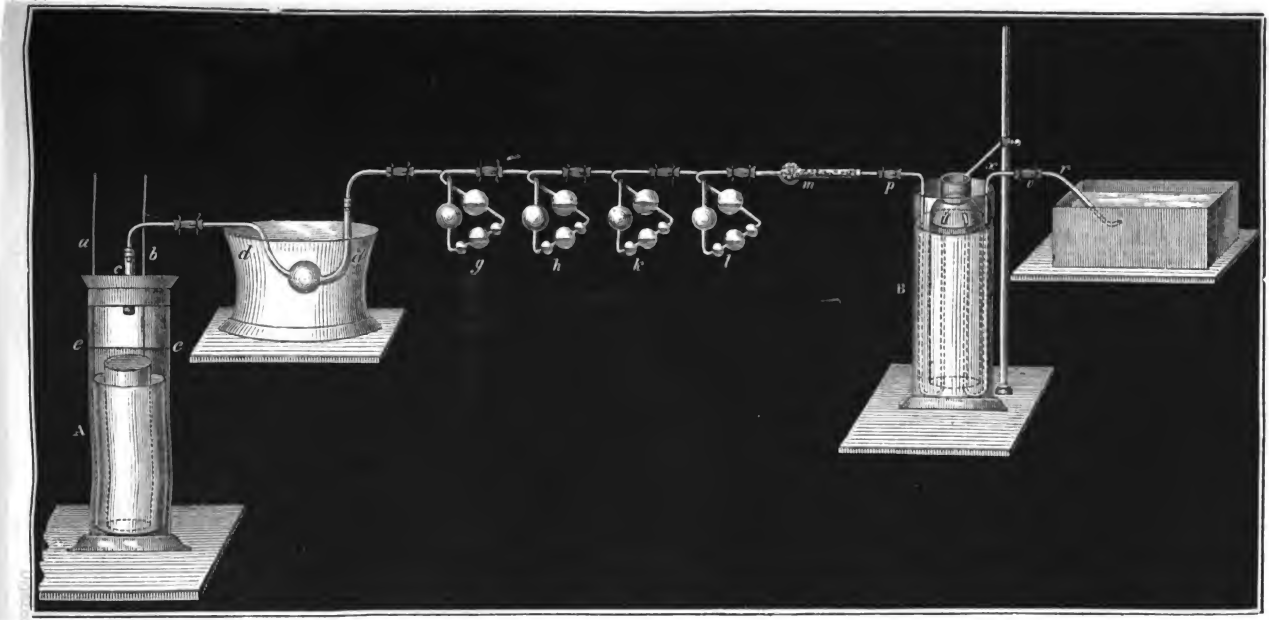
* The presence of chloride of potassium gives rise to the formation of secondary chlorinated products requiring more minute investigation. The soda salt cannot be employed with advantage, inasmuch as the bicarbonate, which is formed during the decomposition, enfeebles to a great extent the electrical current, interrupting it entirely towards the end of the process. The bicarbonate of potash being more soluble, a few crystals only separate during the decomposition.

† The plate containing the figures here described, not having been sent with the manuscript, is unavoidably omitted in this number of the Journal, but will appear with the next.



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the copper by a narrow ring of glass, placed between the two cylinders at their lower extremities. Both wires, as well as the large delivery tube *c*, are cemented perfectly air tight into the cork, the tube being of sufficient diameter to admit of emptying and filling the cylinder without inconvenience.

On passing the electrical current, produced by four elements of Bunsen's zinco-carbon battery, through the apparatus filled to the height *c c*, with a concentrated solution of valerianate of potash, the platinum wire *b* forming the positive pole, the negative wire being in connexion with the cylinder of copper, the following phenomena are observed: A lively evolution of gas takes place simultaneously with the formation of yellowish oily drops, possessing an agreeable etherial odour; on agitation with the liquid, the oil remains undissolved, even on the addition of potash.

The remarkably odorous gases which are evolved during the process, contain, after complete expulsion of air from the apparatus, no longer a trace of oxygen, and may be ignited without fear of explosion. Carbonic acid and hydrogen, however, are present in considerable quantities, in conjunction with a third gas burning with a highly luminous flame, and imparting to the mixture its peculiar odour.

After the action of the current had been continued for several hours, the stratum of oily liquid on the surface had increased to the height of several lines, while the valerianate of potash was almost completely converted into a mixture of carbonate and bicarbonate of potash, the latter generally crystallizing towards the end of the operation.

With a view of ascertaining at which pole each of these products was liberated, I endeavoured to separate the electrodes by means of a porous diaphragm, which allowed me to collect separately the substances disengaged at either pole. I employed for this purpose a porous cell of clay, into which a small glass tube of nearly equal diameter, and open at both ends, was fastened air tight by means of a caoutchouc joint. This arrangement containing the platinum foil, forming the positive pole, and admitting of being closed by a cork furnished with a delivery tube, was introduced into the copper cylinder of the decomposing apparatus.

Both cylinders were now filled with a solution of the neutral valerianate to the height of about one inch above the caoutchouc joint. It was found that on closing the circuit, only hydrogen and free potash were disengaged at the copper pole, while all the other products, the etherial oil, carbonic acid, the odorous gas, and the free acid, (which, in this arrangement, prevented the formation of a carbonate,) appeared at the positive pole.

VALYL.

In the experiments instituted for the preparation * of the etherial oil, I preferred removing the product from time to time with a pipette, which I introduced through the open glass tube *c*, the process being continued until the solution was entirely exhausted of valerianic acid.

The alkaline residue was now again introduced into a porcelain dish, and neutralized with pure valerianic acid; the neutral solution being again repeatedly subjected to the process of electrolysis, until a sufficient quantity of oil had been collected.

The impure product, after repeated agitation with water, exhibits the following properties: It is miscible with alcohol and ether in all proportions, insoluble in water, and of lower specific gravity than that liquid. It possesses an agreeable etherial odour. Chloride of calcium is dissolved by it, particularly in the cold, and hence the slight turbidity which is observed when the clear anhydrous liquid is subjected to ebullition. It commenced boiling a few degrees above 100° (212° F.), the temperature rapidly rising to 160° (320° F.) and even higher; the last products possess a penetrating disagreeable odour, and differ in a remarkable manner from the liquid which passed over at a lower temperature. The quantity of carbon found in the distillate, collected at different temperatures, diminishes with the rise of the boiling point, decreasing from 80 to 76 per cent., while the amount of oxygen, varying between 6 and 10 per cent, is found in the inverse proportion. The disagreeably smelling oil distilling towards the end of the operation, appears to be formed only by the action of chloride of calcium on the original compound; but even when distilled in vacuo at very low temperatures, the distillates collected at different stages of the process exhibit a composition not less variable.

It appears that the impure oil is a mixture of at least two substances, its deportment with an alcoholic solution of potash affording a powerful argument in favour of this opinion.

On boiling a mixture of this oil with an alcoholic solution of potash in a flask connected with the lower extremity of a Liebig's condenser, placed in such a position as continually to return the condensed products to the boiling fluid, the following phenomena are observed. Immediately on the application of heat, bubbles of a gaseous body are seen to rise, possessing the characteristic odour of the compound, which, in the electrolytical decomposition of valerianate of potash, accompanies the evolution of hydrogen and carbonic acid: hence, it appears that this gas, which is held in solution by the liquid, becomes liberated when heat is applied. In a short time the evolution ceases, and the odour of the gas is no longer perceptible; when in a full state of ebullition the oil, previously colourless, assumes a yellowish tint, and becomes slightly turbid, while a heavy, apparently oily liquid collects at the bottom of the flask, which on examination is found to be an aqueous solution of valerianate of potash. To effect complete decomposition of the constituent affected by potash, at least half an hour's ebullition is necessary.

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* The decomposing apparatus employed in this and the following experiments, was placed in a vessel of water at the temperature of 0° C. The solution of valerianate of potash being moderately heated, hardly a trace of the oil is produced, the decomposition taking place in an entirely different manner.

On mixing the liquid after boiling, with a large excess of water, a light etherial oil separates, which, after standing for some time, collects on the surface into a clear transparent layer; repeatedly washed with fresh portions of water, and subsequently dried by chloride of calcium it exhibits a pretty constant boiling point at 108° (226·4 F.). The fraction distilling at this temperature, when subjected to a second rectification boiled at the same point, the first three-fourths of the product being collected. The quantity of pure substance thus obtained exceeds half the original volume of the impure oil. The purified compound presents itself in the form of a clear pellucid fluid of agreeable odour, and first insipid, though afterwards of a burning taste; miscible with alcohol and ether in all proportions, it is perfectly insoluble in water, which readily precipitates it from its alcoholic and etherial solutions. It boils exactly at 108° (226·4° F.), distilling without change to the last drop. It is inflammable, and burns with a strongly luminous smoky flame. It dissolves chloride of calcium, but to a less extent than the impure oil. Its specific gravity at 18° (64·4 F.) is 0·894, that of the vapour being 4·053.

By combustion with oxide of copper* the following results were obtained:

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* It is impossible to burn this substance, so rich in carbon, with either protoxide of copper or chromate of lead alone, a small quantity of metallic carbide being formed, which occasions a deficiency in the carbon amounting to between 0·5 and 0·8 per cent; hence combustion with oxygen is absolutely necessary, the latter being conveniently evolved from small pieces of perchlorate of potash placed at the posterior end of the combustion tube, a plug of dry asbestos preventing contact with the protoxide of

I. 0·1825 grm. of substance gave
0·5630 ,, ,, carbonic acid, and
0·2610 ,, ,, water.
II. 0·1578 ,, ,, substance gave
0·4855 ,, ,, carbonic acid, and
0·2260 ,, ,, water.

These numbers lead to the formula

$$C_8 H_9$$

	Theory.		Experiment.	
8 equiv. of Carbon .	600·0	84·2	84·1	84·0
9 ,, ,, Hydrogen .	112·5	15·8	15·9	15·8
	712·5	100·0	100·0	99·8

This compound possesses the composition of the, hitherto hypothetical, radical of the still unknown alcohol belonging to butyric acid ($C_8 H_9 O, HO$), or the radical which, in valerianic acid, we assume to be in combination with oxalic acid. I propose to call it valyl.

Without entering here minutely into the question, whether valyl is indeed the radical of an alcohol corresponding to methyl, ethyl, and amyl; I will only mention one fact, which, in support of such a supposition, may seem of some importance; viz. that the specific gravity of its vapour exactly coincides with the number indicated by theory. According to the analogy of the methyl and ethyl series this compound would contain 4 vol. of carbon vapour, and 9 vol. of hydrogen condensed into 1 vol., hence the density of its vapour would be 3·9387, viz.:

4 vol. of Carbon	3·3168
9 ,, ,, Hydrogen . . .	0·6219
1 vol. of Valyl.	3·9387

Experiment gave the following results:

Substance employed	0·2085 grm.
Volume of vapour observed . .	63·3cc
Temperature	133·3° C.
Barometer	752·9mm
Mercury-column	64·0mm
Pressing oil-column at 17°C . .	262·0mm

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copper. In addition to this precaution, it is necessary to attach to the common bulbs a tube containing solid potash, in order to absorb the aqueous vapour volatilized in the, gases passing through the potash apparatus.

The specific gravity of valyl vapour as calculated from the foregoing numbers is 4·053, closely coinciding with the theoretical value.

Valyl is difficultly acted on by oxidizing agents; moderately strong nitric acid, or a mixture of chromate of potash and sulphuric acid have very little action upon it even after continuous ebullition; strong fuming nitric acid, however, especially after the addition of sulphuric acid, completely oxidizes this compound, nitrous fumes being evolved, while the oil gradually disappears. On neutralizing with carbonate of baryta, evaporating the filtrate to dryness, and extracting the residue with strong boiling alcohol the nitrate of baryta remains undissolved. The alcoholic liquid when evaporated leaves a saline residue, the distillation of which, with sulphuric acid, yields a yellow acidulous liquid, possessing in an eminent degree, the characteristic odour of butyric acid. On neutralizing the solution with freshly precipitated carbonate of silver, and filtering whilst boiling, a crystalline silver salt is deposited on cooling, which is readily darkened by exposure to light, or by continued ebullition with the mother liquor. The dry salt does not detonate when heated. The potassium, barium, and lead salts, do not appear to crystallize; want of material has prevented me from determining the composition of this acid, and of its salts by analysis; considering, however, the mode of its formation, the peculiar and unmistakeable odour of butyric acid, and its yellow colour, it becomes very probable that this compound is a mixture of butyric acid, and of nitrobutyric acid.

$$HO, C_6 \left\{ \begin{matrix} H_6 \\ NO_4 \end{matrix} \right\} C_2 O_3$$

corresponding to nitro-metacetonic acid.

The following equation represents the transformation of valyl into butyric acid.

$$\underbrace{C_8 H_9}_{\text{Valyl.}} + 5\,O = \underbrace{HO, (C_6 H_7)\, C_2\, O_3}_{\text{Butyric acid.}} + HO.$$

Dry chlorine has no action on valyl in the dark, the minutest ray of light, however, suffices for the immediate production of hydrochloric acid vapours, while chlorinated substitution compounds are simultaneously formed. By an excess of chlorine the liquid gradually becomes converted into a semi-fluid almost viscid mass: direct combination of chlorine and valyl, without elimination of hydrogen does not occur under these circumstances.

The action of bromine on valyl, although less powerful, is attended with similar phenomena; iodine is dissolved in considerable quantity by it without however entering into combination; sulphur likewise has no action upon it.

The decomposition of valerianic acid into valyl and carbonic acid, with the simultaneous evolution of hydrogen is represented by the following equation:

$$\underbrace{HO, (C_8 H_9) C_2 O_3}_{\text{Valerianic acid.}} = \underbrace{C_8 H_9}_{\text{Valyl.}} + 2 CO_2 + H.$$

which is so extremely simple, that further elucidation would be superfluous were not other products formed at the same time. In order clearly to understand this peculiar reaction, we must direct our attention to the study of the two bodies occurring with it; viz.: the oxygenated constituent of the impure oil, and the odorous gas evolved with the carbonic acid. If we consider the fact of the elimination of valyl at the oxygen pole of the battery, the idea naturally suggests itself, that a partial oxidation of it into oxide of valyl may there be effected; the supposition, however, that the original oil consists of a mixture of valyl and its oxide is immediately discountenanced by its peculiar deportment with an alcoholic solution of potash, unable, as we are, to understand what kind of compound would be thus produced. The potash solution with which the oil had been boiled, when diluted with water to separate the valyl, evaporated to dryness, and distilled with sulphuric acid, was found to contain a considerable quantity of valerianic acid. The presence of this acid may be most easily explained, by assuming the existence and decomposition in the liquid, of a valerianic ether, an assumption which would lead us to consider the oxygenated constituent of the original oil as valerianate of oxide of valyl. The formation of this ether will be easily understood, if we bear in mind, that together with valyl and oxygen, valerianic acid is likewise liberated at the positive pole simultaneously with oxide of valyl in the nascent state.

It is true, that in the above decomposition by an alcoholic solution of potash, according to the analogy of the compound ethers generally, hydrated oxide of valyl should have been liberated.

If, however, and it can hardly be doubted, the hydrated oxides of amyl, valyl, and ethyl, present the same relation with reference to their miscibility with water, as do valerianic, butyric, and acetic acids, the ratios of whose solubility are inversely as their atomic weights, it is at once intelligible why, with so small a quantity of substance at my disposal, I did not succeed in separating the hydrated oxide of valyl from a liquid containing alcohol in solution.

The presence of this compound, however, was proved to a certain extent by the following observations. The alcohol containing valerianate of potash was diluted with water to separate the valyl, and distilled off from the valerianate. On introducing the first portion of the distillate into a boiling mixture of bichromate of potash and dilute sulphuric acid, a product passed over, possessing in an eminent degree the characteristic odour of both butyric and acetic acids. A further confirmation of this view of the composition of the crude oil is afforded by analysis.

The substance for investigation was repeatedly washed with water, (first with a dilute alkaline solution), dried over chloride of calcium, and distilled in vacuo at a low temperature.

0·1175 grm. of the distillate gave
0·3320 „ „ carbonic acid, and
0·1475 „ „ water.

corresponding to the following composition per cent.:

Carbon . . .	77·0
Hydrogen . .	13·8
Oxygen . . .	9·2
	100·0

If, starting with the formula $C_8\ H_9\ O$, $(C_8\ H_9)\ C_2\ O_3$ for the oxygenated oil, we calculate from the quantity of oxygen found, the per-centage of carbon and hydrogen belonging to this compound, we arrive at the following composition:

18 equivs.	Carbon . . .	31·0
18 „	Hydrogen . .	5·1
4 „	Oxygen . . .	9·2
		45·3

by subtracting these numbers from the above we obtain carbon and hydrogen exactly in the proportion required by the composition of valyl $(C_8\ H_9)$.

	Experiment.	Theory.
Carbon . . .	46·0	46·1
Hydrogen . .	8·7	8·6

A similar mixture, prepared at a different period, when subjected to combustion gave the following numbers:

0·2647 grm. of substance gave
0·7600 „ „ carbonic acid, and
0·3420 „ „ water.

and a similar calculation leads us to the following results:

	Experimental per-centage.		Composition of valerianate of valyl.		Composition of valyl.	Theory.
Carbon . .	78·3	minus	25·0	=	53·3	53·4
Hydrogen .	14·3		4·2		10·1	10·0
Oxygen . .	7.4		7·4			
	100·0		36·6		63·4	63·4

It now only remains to determine the nature of the gas evolved with carbonic acid, in the decomposition of valerianate of potash. In order to separate this gas from the vapour of valyl evaporated with it, as well as from carbonic acid, I passed it from the decomposing apparatus through a system of tubes, (*fig.* 1). *d d* is an empty tube blown out to a bulb in the lower part, and surrounded by a frigorific mixture. In this tube the larger quantity of valyl vapour is condensed, a small portion which may have escaped liquefaction being arrested in a Liebig's apparatus *g,* filled with alcohol, the vapours of which are condensed in a similar apparatus *h* containing water. The two following bulbs *k* and *l* are filled with a solution of potash, while the tube *m* contains potash in the solid form, serving, both for the separation of carbonic acid, and for the complete dessication of the gas. Finally, to obtain a perfect mixture, the evolved gases were collected in the gas-holder *B,* which consists of a cylinder of glass, 3 inches in diameter, and 11 inches in height, containing an inverted bell-jar, open at the lower extremity, and enclosing one vertical branch of each of the two U-shaped tubes *s* and *x*. The bell-glass is fixed by a holder in its lowest position, and the apparatus filled with mercury to such an extent, that the two tubes through which the air contained in the bell-jar is expelled, rise only a few lines above its surface. The tube *s,* moreover, at its horizontal extremity is connected by an air-tight caoutchouc joint with the tube *m,* while the branch *x* communicates in the same manner with the delivery tube *r,* which may be opened or closed at pleasure by depressing or elevating it from the mercury of the trough; both the connectors being, moreover, furnished with caoutchouc valves.

When the evolution of gases, occasioned by closing the galvanic circuit in the decomposing apparatus, had lasted nearly half an hour without interruption, and all the air contained in its different parts had evidently been expelled, the caoutchouc valve *v* was closely tied, while the holder with which the bell-jar had been depressed in the mercury, was gradually elevated as the vessel became filled with the gas generated by the decomposition. When a sufficient quantity of gas had been collected in this manner, the evolution was interrupted by breaking contact. By now tying the valve *p*, the gases contained in the gas-holder were no longer in connexion with the generating apparatus. By opening the valve *v*, and depressing the bell-jar, the quantity of gas required could easily be collected over mercury, and then transferred into the eudiometer, or into the glass balloon, for the determination of its specific gravity.

In determining the specific gravity, the following numbers were obtained:

Vol. of gas in balloon . . .	15° C.	755·9mm	86·4 c. c.
Weight of balloon filled with gas	15° „	771·0 „	61·628 grm.
„ „ „ air	15° „	771·0 „	61·672 „

From the above numbers, the specific gravity is calculated as 0·604.

In performing the eudiometrical analysis, I availed myself of the circumstance of the odorous constituent being absorbed by sulphuric acid. I therefore introduced into a measured volume of the gas a coke ball, saturated with strong fuming acid; the sulphurous acid, together with the sulphuric vapours, being subsequently removed by a moistened ball of potash.

In this manner, the following numbers were obtained:

I.

	Vol. observed.	Temp.	Bar.	Height of mercury above level in the trough.	Corrected vol. 0° C. 1m. Press.
Original vol. (dry)	117·7	9·9	765·9mm	65·0mm	79·6
After absorption with sulphuric acid and potash (dry)	88·8	9·0	761·1 „	93·3 „	57·4

The quantity of odorous substance in the mixed gases absorbable by sulphuric acid, consequently amounts to 27·8 per cent.

The residual gas, no longer possessing any odour, and burning with a pale blue, non-luminous flame, was transferred into a eudiometer furnished with platinum wires, and exploded with oxygen, when it was found to consist of pure hydrogen.

Another portion of the above mixture, when exploded with oxygen, gave the following results:

II.

	Vol. observed.	Temp.	Bar.	Height of mercury above level in the trough.	Corrected vol. 0° C. 1m. Press.
Original vol. (moist).	111·8	11·0	759·4mm	353·7mm	42·4

After admission of oxygen (moist).	324·6	11·1	759·3^{mm}	141·9^{mm}	189·5
After combustion (moist).	222·7	11·1	759·0 „	242·3 „	108·4
After absorption of CO_2 (dry).	146·0	13·0	759·1 „	318·2 „	61·4

The gas remaining after the absorption of carbonic acid consisted only of pure oxygen, as had been ascertained in a previous experiment.

The above analysis leads to the following results:

	Volume of combustible gas.	Oxygen cons^d.	Carbonic acid prod^d.
	42·4	85·7	47·0
or			
	100·0	202·1	110·8

The mixture of gases under investigation containing, according to experiment II, 72·2 per cent. of hydrogen, requires 36·1 vol. of oxygen for its combustion; it is therefore evident that the remaining 27·8 vol. require 166 (= 202·1 — 36·1) vol. of oxygen, in order to produce 110·8 vol. of carbonic acid. These numbers stand very nearly as, 1 : 6 : 4, or, in other words, 1 volume of the odorous gas requires 6 vol. of oxygen to produce 4 vol. of carbonic acid. Four vol. of carbonic acid consisting, however, of 2 vol. of carbon and 4 vol. of oxygen, and altogether 6 vol. of oxygen having disappeared, 2 vol. having evidently served for the combustion of 4 vol. of hydrogen, it is obvious that the odorous gas contains 2 vol. of carbon and 4 vol. of hydrogen condensed into one volume; hence its specific gravity is, 1·934.

2 vol. of Carbon vapour . .	1·658
4 „ „ Hydrogen . .	0·276
1 „ „ $C_4 H_4$ . . .	1·934

According to the above experiment, the specific gravity of a mixture of 72·2 vol. of hydrogen, and 27·8 vol. of the carbo-hydrogen, is equal to 0·604; hence it follows that the specific gravity of the latter alone is, 1·993, closely coinciding with the result of experiment.

The odorous carbo-hydrogen evolved at the positive pole in the electrolytical decomposition of valerianate of potash, according to these experiments, exhibits the composition of olefiant gas, but possesses a specific gravity double that of this compound. In this respect, it agrees with the carbo-hydrogen discovered by Faraday, and named by Berzelius *ditetryl*, with which it, in fact, appears identical by its comportment with chlorine.

If the mixed gases, washed with potash and alcohol, and collected in the gas-holder, be passed through a chloride of calcium tube into a flask (provided with three tubulures, one of which terminates in a narrow aperture), and mixed with perfectly dry chlorine, an excess being carefully excluded and light as much as possible avoided, the sides of the flask become quickly covered with oily drops, which soon collect into larger globules, and flow out from the lower aperture, while hydrochloric acid, formed by the direct combination of chlorine with the free hydrogen, is disengaged. During the whole process a slight evolution of heat is perceptible.

About half an ounce of the oily liquid, which had been collected in the vessel placed under the lower aperture of the flask, was first treated with slightly alkaline, and afterwards with pure water, in order to separate dissolved hydrochloric acid; it was then dried over fused chloride of calcium, and subjected to a fractional distillation. The portion which boiled between 125° C. (257° F.) and 130° C. (266° F.) forming by far the larger quantity, was separately collected and purified by repeated rectifications, when a nearly constant boiling-point at 123° C. (253·4 F.) was obtained.

This compound possesses the following properties. It is a clear colourless etherial liquid, insoluble in and heavier than water. It has an agreeable sweetish odour and taste, deceptively similar to that of Dutch liquid. It dissolves with facility in alcohol and ether, and boils at the constant temperature of 123° C. (266° F.); mixed with alcohol it burns with a luminous smoky flame, with evolution of hydrochloric acid. Its specific gravity at 18° C. (64·4 F.) is 1·112, the density of its vapour 4·426, the latter being calculated from the following data:

Substance employed	0·244 grm.
Vol. of vapour observed	67·7 c. c.
Temperature	139·0° C.
Bar. pressure	751·0 mm.
Col. of mercury to be deducted	51·0 „
Pressure of oil col. at 17° C.	366·0 „

By combustion with protoxide of copper the following results were obtained:

I. 0·3990 grm. of substance gave:
0·5590 „ „ carbonic acid, and
0·2470 „ „ water.

II. 0·2165 „ „ passed over ignited lime, dissolved in nitric acid and precipitated with nitrate of silver gave:
0·4790 „ „ chloride of silver.

These numbers coincide with the formula:

$$C_4\,H_4\,Cl, \text{ or } C_8\,H_8\,Cl_2.$$

	Theory.		Experiment
8 equiv. of Carbon . .	600·0	37·8	38·2
8 „ „ Hydrogen .	100·0	6·3	6·8
2 „ „ Chlorine . .	886·0	55·9	55·5
	1586·0	100·0	100·5

If we adopt, in this compound, a similar condensation of the elements, as in the oil of olefiant gas, the specific gravity of its vapour should be, 4·3837.

2 vol. of Carbon . .	1·6584
4 „ „ Hydrogen . .	0·2764
1 „ „ Chlorine . .	2·4489
1 „ „ the new Chloride .	4·3837

(with this number the result of experiment 4·426 closely coincides).

It would have been extremely interesting to have studied the comportment of this compound with an alcoholic solution of potash, since its analogy to chloride of elayl justifies the expectation that, in this case, chloride of potassium, and a compound corresponding to chloride of acetyl would have been formed, the latter being represented by the formula:

$$C_8\left\{\begin{matrix}H_7\\Cl\end{matrix}\right\}$$

The small quantity of liquid at my disposal, unfortunately, did not allow me to pursue the subject any further. I must therefore confine myself to mentioning, that on heating an alcoholic solution of the compound with potash, a copious crystalline precipitate of chloride of potassium was formed, while the characteristic odour of the compound was replaced by that of a very volatile liquid, having probably the formula:

$$C_8\left\{\begin{matrix}H_7\\Cl\end{matrix}\right\},$$

which remaining dissolved in the alcoholic solution, was precipitated, on the addition of water, in small drops, which separating at the sides of the vessel, united only with difficulty; the liquid remaining milky for a considerable period.

By the action of chlorine, on the above carbo-hydrogen, with the fluid boiling at 123° C. (253°·4 F.), higher chlorinated products are formed, even when an excess of chlorine has been carefully avoided. The slow elevation of the boiling-point from 123° C. (253°·4 F.) to 160° C. (320° F.), at once intimates that we have, in this case, other substances richer in chlorine, which possibly might have been separated by fractional distillation of a larger quantity.

The combustion of 0·3620 grm. of the product, distilling at 132° C. (269°·6 F.), gave 0·4600 grm. of carbonic acid, and 0·1800 grm. water, corresponding to the following per-centage composition:

Carbon . . .	34·6
Hydrogen . .	5·5

A compound still richer in chlorine is obtained by passing the gas through pentachloride of antimony, and distilling the substance thus produced. During the process of absorption, the mixture blackened, with the evolution of hydrochloric acid. The oily product obtained was purified by repeated distillation with water, dried over chloride of calcium, and subjected to analysis, when it exhibited the following per-centage composition:

Carbon . . .	28·4
Hydrogen . .	4·0
Chlorine . .	68·2

being evidently a mixture of different chlorinated compounds, whose composition may be represented by the general formula:

$$C_8\,H_{(8-x)}\,Cl_{(2+x)}$$

The opinions of chemists regarding the rational composition of the oil of olefiant gas, are, as is well known, still divided, as to whether it should be considered as the chlorine compound of a radical $C_2\,H_2$, or whether its atomic weight should be doubled, in which case it would appear as the hydrochlorate of chloride of acetyl.

$$C_4\left\{\begin{matrix}H_3\\Cl\end{matrix}\right\},\ H\,Cl.$$

This question must remain undecided as long as both views can still claim arguments of equal force. Now, whichever of these opinions may in future be found correct, it will evidently determine our views respecting the chemical constitution of the above chlorinated oil produced from ditetryl, or, in other words, it will decide whether we have to adopt the formula:

$$C_4\,H_4\,Cl, \text{ or } C_8\left\{\begin{matrix}H_7\\Cl\end{matrix}\right\},\ H\,Cl,$$

as the true exponent of its rational composition. This supposition once recognised will add new force in favour of the latter mode of representation, if we bring to bear upon this case the law of Kopp respecting the regularity displayed in the boiling points of *homologous* liquids, (to employ an expression lately introduced to designate the members of such series of bodies), which, like the alcohols or the fatty acids, are represented as being derived from a starting member by the addition of n times $C_2\,H_2$, $C_4\,H_2$, on any other carbo-hydrogen, experiment having (within certain limits) evinced the fact that the boiling points of homologous fluids rise 19° C. (34° F.) for each additional equivalent of the carbo-hydrogen $C_2\,H_2$. The chloride of ditetryl, $C_4\,H_4\,Cl$, which boils at 85° C. (185° F.), differing from chloride of elayl by one equivalent of the carbo-hydrogen $C_2\,H_2$, should boil at 104° C. (219°·2 F.); on doubling, however, the atomic weight of the two bodies, (chloride of elayl $C_4\,H_4\,Cl_2$, and chloride of ditetryl $C_8\,H_8\,Cl_2$), their elementary difference becoming equal to 2 $(C_2\,H_2)$, the boiling point of the latter should be 123° C. (253°·4 F.), which is the temperature actually observed by experiment. Although this observation cannot be considered as a direct argument for the assumed molecular arrangement, I consider it nevertheless of sufficient weight to assist in the ultimate decision of the question regarding the atomic constitution of the two compounds.

We find no difficulty in explaining the formation of the carbo-hydrogen $C_4\,H_4$, or $C_8\,H_8$, from valerianic acid; like the valerianate of the oxide of valyl, it is evidently a secondary product of the decomposition of valyl, and most probably formed by the action of the oxygen separating along with valyl, at the positive pole. We may assume that, under the influence of this oxygen, valyl is deprived of one equivalent of hydrogen, yielding one equivalent of ditetryl and one equivalent of water.

The action of electrolized oxygen, on a solution of valerianate of potash, therefore gives rise to three distinct phenomena:

1st. A decomposition of the acid into valyl and carbonic acid:

$$\underbrace{HO,\,(C_8\,H_9)\,C_2\,O_3}_{\text{Valerianic acid.}} + O = \underbrace{C_8\,H_9}_{\text{Valyl.}} + 2\,CO_2 + HO.$$

2ndly. The decomposition of valyl into ditetryl and water:

$$\underbrace{C_8\,H_9}_{\text{Valyl.}} + O = 2\ (\underbrace{C_4\,H_4}_{\text{Ditetryl.}}) + HO.$$

3dly. A direct oxidation of valyl into oxide of valyl, which combines in the nascent state with free valerianic acid.

$$\underbrace{C_8\,H_9}_{\text{Valyl.}} + O + \underbrace{(C_8\,H_9)\,C_2\,O_3}_{\text{Valerianic acid.}} = \underbrace{C_8\,H_9\,O,\ (C_8\,H_9)\,C_2\,O_3}_{\text{Valerianate of oxide of valyl.}}.$$

The two latter processes appear to take place simultaneously, though perfectly independent of each other. I have not, however, succeeded in exactly ascertaining the circumstances which favour the formation of the one or the other.

ELECTROLYSIS OF ACETIC ACID.

The remarkable analogy of the series of acids $(C_2\,H_2)_n + O_4$, induced me to believe that acetic acid would undergo a similar decomposition to valerianic acid, yielding, by absorption of one equivalent of oxygen, methyl and carbonic acid:

$$\underbrace{HO\,(C_2\,H_3)\,C_2}_{\text{Acetic acid.}}\,O_3 + O = \underbrace{C_2\,H_3}_{\text{Methyl.}} + 2\,CO_2 + HO.$$

In a preliminary experiment, it was found that on decomposing a concentrated solution of acetate of potash, gaseous products only were evolved, consisting of carbonic acid, hydrogen, a combustible inodorous gas, and a compound possessing a peculiar etherial odour, and absorbable by sulphuric acid. In the investigation of these gaseous products, I availed myself of the same decomposing apparatus as was employed in the decomposition of valerianic acid; the evolved gases were first passed through a series of bulb tubes containing potash, afterwards through a tube filled with sulphuric acid (for the absorption of the odorous gas), and finally made to pass through a tube containing pieces of fused hydrate of potash, previous to collection in a gas-holder. In this operation it is necessary to employ a very concentrated solution of the potash salt perfectly free from chloride of potassium, the smallest trace of the latter giving rise to the formation of chloride of methyl, which is easily recognisable by the green-bordered flame with which it burns when inflamed in contact with the air.*

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* In a similar manner various other secondary products are formed, a mixture of

When the evolution of gas had continued for about an hour, and had entirely displaced all traces of atmospheric air contained in the system of tubes and the gasometer, I filled the latter by gradually raising the bell, the delivery tube dipping under the mercury. The apparatus being too small to allow a sufficient quantity of gas being collected for taking its specific gravity, for eudiometrical analysis, and for combustion with protoxide of copper, the bell-jar was again fixed before being completely filled, and the gas issuing from the tube *r* was collected in a flask, for the determination of the specific gravity.

The contents of the gasometer were now easily confined by tying the caoutchouc valves *p* and *v* over the inserted glass rods, after the collection of gas had ceased from the interruption of the galvanic current.

In determining the relative proportion of carbon and hydrogen, an ordinary combustion-tube, open at both ends, was employed; when filled with freshly ignited protoxide of copper, the anterior extremity was connected with the usual potash bulbs and chloride of calcium tube, the posterior end being attached by a caoutchouc tube to the gasometer. After opening the caoutchouc valve *v*, the silken cord was untied, and by gently depressing the bell-jar, a continuous stream of gas passed over the ignited protoxide of copper, until a sufficiency of carbonic acid and water had been collected, when the caoutchouc valve was again closed. The posterior tube connected with the gas-holder was now cut, in order to allow of the removal of the carbonic acid remaining in the apparatus.

The following are the numbers obtained:

Carbonic acid . .	0·2470
Water	0·2635

corresponding to a ratio of 1 equivalent of carbon to 2·06 equivs. of hydrogen, or of 1 volume of carbon vapour to 5·2 vols. of hydrogen.

The specific gravity of the gas collected in a small flask over mercury was found to be 0·403.

	Temp.	Pressure.	
Volume of gases in flask . . .	19·3°C.	749·2$^{\text{mm}}$	211·3 c c.
Mercury column to be deducted .	..	15·0 „	..
Weight of flask filled with gas .	22·0°C.	749·0 „	46·669 grm.
Weight of flask filled with air .	—	—	46·819 „

valerianate of potash and chloride of potassium, for example, produces in the place of valyl, a chlorinated, etherial compound; a disagreeably smelling compound is obtained by exposing a mixture of acetate of potash and sulphide of potassium to the action of a galvanic current, the anode being formed of a platinum plate.

The further data for the composition of the gas were obtained by eudiometrical analysis, which exhibited the presence of a minute quantity of oxygen.

	Observed.	Temp.	Bar.	Height of mercury column.	Corrected vol. 0°C. and 1^{m} pressure.
Volume of gas employed (moist).	137·3	19·3°C.	747·2^{mm}	31·5^{mm}	89·6
After absorption of oxygen (moist).	132·0	19·0° ,,	740·0 ,,	35·9 ,,	86·9

The quantity of oxygen, therefore, amounts to 3 per cent. The residuary gas was transferred into a larger eudiometer, and detonated with oxygen in experiments II *a.* and II *b.*, the following numbers were obtained:

II *a.*

	Observed vol.	Temp. C°	Barom.	Height of mercury column.	Corrected vol. 0° C. and 1^{m} pressure.
Volume of gas employed (moist).	200·0	18·0	749·0^{mm}	373·4^{mm}	67·6
After admission of oxygen (moist).	475·9	17·4	751·2 ,,	92·3 ,,	287·6
After combustion (moist).	345·6	18·0	751·1 ,,	225·6 ,,	165·4
After absorption of carbonic acid (dry)	283·2	17·7	748·8 ,,	288·6 ,,	122·3
After admission of hydrogen (dry).	574·5	17·8	747·5 ,,	6·0 ,,	399·0
After combustion (moist).	114·2	17·4	748·9 ,,	460·2 ,,	29·4

II *b.*

Volume of gas employed (moist).	91·8	18·9	740·2 ,,	476·3 ,,	21·26
After admission of oxygen (moist).	410·2	19·0	740·3 ,,	153·7 ,,	218·7
After combustion (moist).	366·2	19·0	740·4 ,,	197·1 ,,	180·43
After absorption of carbonic acid (dry).	341·4	18·0	744·0 ,,	222·1 ,,	167·15

	Vol. of gases used.	Oxygen consumed.	Carbonic acid generated.
Experiment II *a*.	67·6	97·7	43·1
Experiment II *b*.	21·26	30·3	13·3

In calculating these numbers for a mixture of hydrogen and methyl, we find that in both experiments a smaller quantity of oxygen has disappeared than is required for the perfect combustion of such a mixture.

This circumstance appears to point out the presence of oxide of methyl, which accompanies methyl itself in pretty constant proportion. In designating the quantity of combustible gas employed by *A*, the oxygen which has disappeared by *B*, the carbonic acid produced in combustion by *C*; and further, the quantity of oxygen, methyl, and of oxide of methyl, respectively by x, y, and z, we arrive at the following equation,

$$\begin{aligned} x + y + z &= \mathrm{A} \\ \tfrac{1}{2}x + 3\tfrac{1}{2}\,y + 3\,z &= \mathrm{B} \\ 2\,y + 2\,z &= \mathrm{C} \end{aligned}$$

by which we obtain for x, y, and z, the following values:

$$x = \frac{2\,\mathrm{A} - \mathrm{C}}{2}$$

$$y = \frac{4\,\mathrm{B} - 2\,\mathrm{A} - 5\,\mathrm{C}}{2}$$

$$z = \mathrm{A} + 3\,\mathrm{C} - 2\,\mathrm{B}.$$

If we now substitute for A, B, and C, the numerical values found, we arrive at the following composition for the two consumed volumes of gas (Exp. II *a* and II *b*):

	Experiment II *a*.	Experiment II *b*.
Hydrogen	46·1	14·60
Methyl	20·0	6·10
Oxide of methyl	1·5	0·56
Total volume	67·6	21·26

Hence, from experiments I. and II., results the following percentage composition of the mixed gases:

Oxygen	3·0	3·0
Hydrogen	66·0	66·6
Methyl	28·8	27·8
Oxide of methyl	2·2	2·6
	100·0	100·0

The specific gravity of a gaseous mixture of this composition would be 0·4123 which closely coincides with the numbers found by experiment, 0·403. This composition receives further confirmation from the relative proportions of carbon and hydrogen, obtained by combustion with protoxide of copper.

			Carbon vapour.	Hydrogen.
28·8 vol.	Methyl	contain	28·8 vol.	86·4 vol.
2·2 „	Oxide methyl	„	2·2 „	6·6 „
66·0 „	Hydrogen	„	— „	66·0 „
The gaseous mixture		. . . .	31·0 „	159·0 „

Being the ratio of 31·0 vol. of carbon vapour to 159·0 vol. of hydrogen, or of 1 vol. of carbon vapour to 5·13 vol. of hydrogen, very closely coinciding with the above experimental ratio of 1 : 5·21.

I have before mentioned, that the gases evolved in the electrolysis of acetic acid, contain a gas which is absorbable by sulphuric acid. Independently of the remarkable odour of acetate of methyl which this gas possesses, the supposition that acetate of methyl is actually obtained among the products of the decomposition of acetic acid, receives some support from the analogous decomposition of valerianic acid. With the view of ascertaining the per-centage of this body in the mixture of gases, and to study its nature, I repeated the above experiments with a portion of gas which had not previously been passed through sulphuric acid, and which consequently still contained the odorous principle; it burned like the other, with a feebly luminous, bluish flame.

An indefinite volume being passed from the gas-holder over ignited protoxide of copper, gave:

0·249 grm. of carbonic acid, and
0·247 „ „ water.

Corresponding to the ratio of:

1 vol. of carbon vapour, and
4·851 vols. of hydrogen.

The specific gravity of the mixture was found to be 0·4373, as is seen by the following experiment:

	Temp. C.	Pressure.	
Volume of gas in flask . . .	18·0°	741·0mm	211·7 cc.
Weight of flask filled with gas .	19·0°	749·0 „	42·4065 grm.
„ „ „ „ „ air	—	—	42·5500 „

To ascertain the per-centage of free oxygen and of the odorous constituent, I first determined, in a measured volume, (experiment III), the quantity of the latter by absorption with a coke ball saturated with sulphuric acid, and subsequently the amount of oxygen, by introducing a ball of phosphorus. The remaining portion of combustible gas was then detonated with oxygen in a large eudiometer, (experiment IV).

III.

	Observed vol.	Temp. C.	Bar.	Height of mercury column.	Corrected vol. 0° C. and 1^{m} pressure.
Volume of gas used (moist).	116·4	17·8	747·2^{mm}	21·2^{mm}	77·67
After absorption with sulphuric acid (dry).	113·8	17·9	746·0 „	24·8 „	77·03
After absorption of oxygen (dry).	113·0	17·6	746·0 „	25·1 „	76·5

IV.

Volume of gas free from oxygen and odorous constituent (moist).	190·6	17·8	746·0 „	378·2 „	63·1
After admission of oxygen (moist).	373·9	17·9	744·7 „	192·4 „	188·4
After combustion (moist).	208·6	18·0	743·8 „	339·6 „	72·17
After absorption of carbonic acid (dry).	105·3	18·2	745·9 „	465·7 „	27·66
After admission of hydrogen (dry).	311·5	18·0	750·6 „	255·7 „	144·63
After combustion (dry).	182·6	18·1	750·6 „	386·5 „	62·35

According to the latter experiment, it follows that 63·1 vols. of gas previously treated with sulphuric acid and phosphorus, require for combustion 97·4 volumes of oxygen, giving rise to the formation of 44·51 vols. of carbonic acid. If we now calculate these numbers according to the above equation for hydrogen, methyl, and oxide of methyl, we find that the original 63·1 vols. contained 40·85 vols. of hydrogen, 20·9 vols. of methyl, and 1·35 vol. of oxide of methyl. From these data, and likewise from the results of experiment III, we obtain the following per-centage composition of the mixture, in which the gas absorbable by sulphuric acid is enumerated as acetate of methyl.

Oxygen	0·7
Hydrogen	63·8
Methyl	32·6
Oxide of methyl	2·1
Acetate of methyl	0·8
	100 0

The specific gravity of such a mixture should be 0·4430, which does not far differ from experimental results, the number obtained being 0·4370.

	Volume per-cent.		Specific gravity.		Weight.
Oxygen	0·7	×	1·1092	=	0·7647
Hydrogen	63·8	×	0·0691	=	4·4086
Methyl	32·6	×	0·0365	=	33·7899
Oxide of methyl	2·1	×	1·5893	=	3·3375
Acetate of methyl	0·8	×	2·5567	=	2·0454

$$\frac{44\cdot3461}{100} = 0\cdot443$$

If we calculate the relative volumes of carbon and hydrogen contained in this mixture of gases, we obtain the following numbers:

			Carbon vapour.	Hydrogen.
63·8 vol.	H	containing	—	63·8 vol.
32·6 „	$C_2 H_3$	„	32·6 vol.	97·8 „
2·1 „	$C_2 H_3 O$	„	2·1 „	6·3 „
0·8 „	$C_2 H_3 O, \bar{A}$	„	1·2 „	2·4 „
Being a proportion of			35·9 to	170·3 „

or of one volume of carbon vapour to 4·74 vols. of hydrogen, which coincides with the results obtained by combustion with protoxide of copper, viz: 1 vol. of carbon vapour to 4·85 vol. of hydrogen. The per-centage composition gains additional support by the eudiometrical analysis of the same gas, which still contained the odorous principle, but which was previously freed from oxygen.

The following numbers were obtained:

V.

	Observed vol.	Temp. C.	Barom.	Height of mercury column.	Corrected vol. 0^0 C. and 1^m pressure.
Volume of gas used (moist).	138·0	18·2	$750·5^{mm}$	$432·6^{mm}$	39·11
After admission of oxygen (moist	360·6	18·3	750·2 „	206·4 „	178·5
After combustion (moist).	263·9	18·2	750·1 „	303·9 „	106·8
After absorption of carbonic acid (dry).	213·9	18·2	748·4 „	354·0 „	78·9

In the combustion of 39·1 vols. of this gas 60·5 vols. of oxygen are consumed, giving rise to the formation of 27·9 vols. of carbonic acid. By now calculating the quantity of oxygen necessary for the combustion of 63·8 vols. of hydrogen, 32·6 vols. of methyl, 2·1 vols. of oxide of methyl, and 0·8 vol. of acetate of methyl, and likewise taking into consideration the amount of carbonic acid produced, we arrive at results but slightly differing from the numbers obtained by experiment:

		Oxygen.		Carbonic acid.
63·8 vols. of H	requiring for combustion	31·9	vols. and producing	—
32·6 „ „ C_2H_3	„ „	114·1	„ „	65 2 vols.
2·1 „ „ C_2H_3O	„ „	6·3	„ „	4·2 „
0·8 „ „ $C_2H_3O, \bar{A}$	„ „	2·8	„ „	2·4 „
99·3 vol. of mixed gases	=	155·1 vols.		71·8 „

or that 39·1 vols. require for combustion 61·0 vols. of oxygen (experimental result, 60·5 vols.), producing 28·2 vols. of carbonic acid (experimental result, 27·9).

These facts sufficiently prove that the quantity of the compound imparting the peculiar etherial odour to the gases, which are evolved in the electrolytical decomposition of acetate of potash, is so small, that if, as experiment seems to point out, it actually consists of acetate of methyl, it becomes almost impossible to condense it by a low temperature. An experiment made with this view was, indeed, perfectly unsuccessful. The ready absorption of this body, by sulphuric acid, agrees with the comportment of acetate of methyl; the acid employed in the experiment assumed a yellowish tint, and darkened on the application of heat, with the evolution of acetic and sulphurous acid vapours.

The above experiments had been completed, when I became aware that a gaseous mixture, consisting of one-third methyl and two-thirds of hydrogen, possesses the same specific gravity as is exhibited by a mixture of two-thirds of marsh-gas, and one-third of hydrogen, and moreover, both mixtures contain the same relative amounts of carbon and hydrogen, and consequently consume, not only an equal volume of oxygen in their combustion, but produce the same quantity of carbonic acid; and hence the facts observed in the electrolysis of acetic acid might lead to the assumption, that the gases evolved in its electrolytical decomposition consist of hydrogen and marsh-gas. With the view of removing all doubt on this point, I have endeavoured to prepare methyl in a state of purity: I availed myself for this purpose, of the decomposing apparatus (*fig.* 2 *b*) already described, which allows us to collect with facility the products liberated at either pole.

The interior cell containing the platinum plate was closed for this purpose with the cork, which besides the platinum wire for producing contact, contained, moreover, the delivery tube through which the generated gases were evolved, in order to be conducted through two bulb-tubes filled with concentrated solution of potash, and afterwards through a similar vessel containing sulphuric acid (for the absorption of water and acetate of oxide of methyl) and subsequently collected in the gas-holder. After every trace of atmospheric air had been expelled, the collected gas contained, nevertheless, a small quantity of carbonic acid, the two potash bulbs not having been sufficient to absorb the carbonic acid, which had been evolved from the separated cell in much larger proportion than in the former arrangement, because, in the former experiment, the simultaneous liberation of acetic acid at the positive pole effectually prevented the formation of a carbonate.

The eudiometrical analysis of the mixture which, as special experiment had proved, did not contain free oxygen, gave the following results:

VI.

	Observed vol.	Temp. C.	Barom.	Height of mercury column.	Corrected vol. 0° C. and 1^{m} pressure.
Volume of gas used (moist).	121·9	17·3	738·6^{mm}	18·2^{mm}	80·9
After absorption of carbonic acid (dry).	90·9	17·2	744·8 ,,	44·9 ,,	59·86

VII.

Gas used (moist).	114·1	17·5	744·9mm	457·4mm	29·23
After admission of oxygen (moist).	452·0	17·5	745·2 „	115·7 „	261·1
After combustion (moist).	374·0	17·6	745·2 „	192·5 „	188·9
After absorption of carbonic acid (dry).	293·5	17·5	746·0 „	273·6 „	130·5

According to these observations the gaseous mixture contains 26·0 of carbonic acid, and 74·0 of combustible gas, of which (experiment VII) 29·23 vols. require 101·37 vols. of oxygen for complete combustion, producing 58·4 vols. of carbonic acid, which closely corresponds with the ratio, 1 : 3½ : 2; hence it appears that the gas evolved with carbonic acid, at the positive pole, is actually methyl, containing not even a trace of marsh-gas, which requires the double volume of oxygen for its complete combustion, and produces only an equal volume of carbonic acid.

The experimental numbers correspond with the following percentage:

Carbonic acid . . .	26·0
Methyl	69·3
Oxide of methyl . .	4·7
	100·0

The specific gravity of such a mixture is 1·188, a number closely coinciding with the result of experiment, which gave 1·172, as the following data will shew:

	Temp.	Barometer.	
Volume of gas in flask . . .	17·3°	717·6	212 c. c.
Weight of flask filled with gas	17·2°	738·6	53·826 grm.
„ „ „ „ air	—	—	53·796 „

The gas remaining after the absorption of carbonic acid (experiment VI), which is methyl mixed with traces of oxide of methyl, possesses the following properties: it is inodorous* and tasteless, insoluble in water, and burns with a bluish non-luminous flame; alcohol dissolves an equal volume, absorbing it without residue; neither sulphuric acid nor pentachloride of antimony dissolve it, and hence it corresponds, in all its properties, to the gas obtained from cyanide of ethyl.*

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* The feebly etherial odour of the gas prepared from cyanide of ethyl evidently arises from traces of cyanide of ethyl.

Methyl may be distinguished from marsh-gas, to which it is in some respects very similar, both by its solubility in alcohol, and its comportment with an excess of chlorine gas, by which methyl is converted into sesquichloride of carbon, while marsh-gas is transformed into the bichloride.

In conclusion, I may observe, that on employing two decomposing cells, the gas evolved at the positive pole does not contain carbonic acid, but consists of pure hydrogen.

According to the observations I have communicated, acetic acid, when decomposed in the circuit of the voltaic current, is decomposed into methyl and carbonic acid, both being liberated at the positive pole, whilst at the negative pole, pure hydrogen only is evolved. It further appears, that a small quantity of methyl is converted into the oxide. On leaving out of consideration the small quantity of the latter, one equivalent of acetic acid should accordingly yield 2 vols. of hydrogen, 2 vols. of methyl, and 4 vols. of carbonic acid, as is shown in the following equation :

$$HO, (C_2\,H_3)\,C_2\,O_3 = \begin{cases} H & 2\text{ vols.} \\ C_2\,H_3 & 2\text{ vols.} \\ 2\,C\,O_2 & 4\text{ vols.} \end{cases}$$

The gases evolved from the decomposing cell, in the decomposition of acetate of potash, should therefore consist of equal volumes of methyl and hydrogen ; as, however, experiments II, IV, and V, show that nearly double the amount of hydrogen is evolved, without an equivalent proportion of oxygen being liberated, we are led to the conclusion, that together with the above-mentioned transformations a simultaneous decomposition of water takes place, whose oxygen (considerably surpassing the amount contained in the oxide of methyl) evidently oxidizes a portion of the liberated methyl completely into carbonic acid and water; from this fact, however, it would follow, that carbonic acid would be produced in much larger proportion compared with methyl, than is indicated by the foregoing formula. With the view of deciding this question, I have investigated the mixture of carbonic acid and methyl, evolved at the positive pole, which had been previously freed from acetic vapours which might have been carried over, by passing the gas through a bulb-tube containing water.

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* Ann. der Chem. und Pharm. Bd. LXV. S. 269.

VIII.

	Observed vol.	Temp. C.	Barom.	Mercury column.	Corrected vol. 0° C. and 1^{m} pressure.
Volume of gas (moist).	110·2	17·0	764·0^{mm}	25·3^{mm}	73·27
After absorption of carbonic acid (dry).	35·3	15·8	753·3 „	99·0 „	21·96

The gaseous mixture under investigation was found to contain 21·96 vols. of methyl and 51·31 vols. of carbonic acid; or, in other words, for every volume of the former, there are 2½ volumes of the latter, instead of 2 volumes, as indicated by the above equation.

These observations appear sufficient to prove, that in the electrolysis of acetic acid, even when employed in the form of a concentrated solution of its potash salt, a simultaneous decomposition of water takes place, which may perhaps be partially or entirely avoided by modifying the electrical current.

Anniversary Meeting, March 30, 1849.

The President in the Chair.

The following Report of the Council was read by the President.

Annual Report of the Council.

We have now, Gentlemen, arrived at our Eighth Anniversary, and it becomes my duty, as the Delegate of your Council, to advert to the general concerns of the Society during the preceding year.

Our Society is at present constituted of one hundred and twelve resident, and one hundred and twelve non-resident Members; three Associates; and nine Foreign Members. In the course of the past year, twenty-nine new Members have been elected: namely, fourteen resident, and fifteen non-resident.

The list of Members deceased during the past year is less extensive than usual, being limited, as I believe, to two individuals; but in one of them, I regret to say, this Society has sustained an especial loss; I allude to the death of one of our original Members, and our late Secretary, Mr. Fownes, which took place at his father's house, at Brompton, on the 31st of last January, before he had completed his 34th year, having been born on the 14th of May, 1815.

Mr. Fownes received his early education first at Enfield, and afterwards at Bourbourg, near Gravelines, in France. He was originally intended for trade, but having an inherent attachment to the pursuits of Science, those of business proved so irksome and distasteful to him, that he was soon induced to relinquish them, and to adopt Chemistry as his profession.

This resolve was materially influenced by his becoming, when about seventeen or eighteen years of age, a member of the Western Literary Institution, where, in conjunction with Mr. Everitt, Mr. Henry Watts, Mr. R. Murray, and others, he established a philosophical class, in which he displayed much readiness as a demonstrator, and great zeal in promoting experimental inquiry.

In January, 1837, he became a pupil of our late colleague, Mr. Thomas Everitt, who then filled the Chair of Chemistry at the Middlesex Hospital; he afterwards visited Germany, and availed himself of the aids of the celebrated school of Giessen, from which he returned with the degree of Ph.D. Soon after his return from Germany, it was his good fortune to become an assistant in the Laboratory of University College, under the tuition of Professor Graham, and he soon showed himself not an unworthy pupil of that eminent master.

From these several sources, Mr. Fownes derived a store of practical and theoretical knowledge, which fitted him to become himself an instructor in the science which he loved, and to which he was now laboriously devoting himself; and he undertook, in the first instance, the Chemical Lectureship at Charing Cross Hospital. In February, 1842, he wrote an Essay on the Food of Plants, which was presented to the Royal Agricultural Society, and to which the prize of that Society was adjudged in December following.—It is an elaborate and valuable paper, and has a place in the Journal of the Society for 1844. In 1842 and 1843 he delivered two short courses of lectures at the Royal Institution. In the summer of 1842, he was appointed the Professor of Chemistry to the Pharmaceutical Society, the duties of which office he entered upon in October of the same year. About this time also he left the Charing Cross Hospital, and upon the death of Mr. Everitt succeeded to the Chemical Lectureship of the Middlesex Hospital; and in addition to these laborious duties, he gave occasional lectures elsewhere, and more especially at the London Institution, where, in the year 1844 he gave a course on Chemical Philosophy. But now it unfortunately became apparent that his health was suffering. With unimpaired mental energies, his bodily strength began to decline, and evident symptoms of pulmonary disease made their appearance, under the form of a troublesome cough and shortness of breath, which rendered lecturing a severe labour, so that in the year 1845 he resigned his office at the Middlesex Hospital, and in the following year was forced to relinquish the duties of his Pharmaceutical Professorship. He was, however, in the meantime, appointed the Professor of Practical Chemistry in the Birkbeck Laboratory at University College, an appointment which he held at the time of his decease. In the summer of 1846, he visited Switzerland, and returned in the autumn in improved health and spirits; but winter again rendered him unable to do the work he wished, and obliged him to desist from those original researches in Organic Chemistry which he had already pursued with so much success, and in which he would doubtless have achieved new and important conquests. The spring of 1847 found him still further worn and exhausted by the ungenial influence of the preceding winter; and though, in the course of the summer he appeared somewhat to rally and improve, it became evident to his medical advisers that he could not, in safety, sustain another English winter; he, therefore, at the suggestion of his friend, Dr. B. Jones, determined upon seeking a warmer climate, and went to Barbadoes. Early in the following spring, he returned to this country; but unfortunately, a severe cold caught on the passage, deprived him of much of the advantage which it was hoped he had derived. His health now began more evidently and rapidly to give way, and he was induced to repair to Torquay, but finding his sojourn there of no avail, he returned to his home at Brompton, where he passed the short residue of his earthly existence.

Mr. Fownes was so well known to the majority of the Members of this Society, that I need say little upon the amiability of his disposition, his disinterested love of science at large, or his skill, his industry, and his success, in that branch of it which he more exclusively adorned, and in which, had it pleased Providence to have extended his sojourn amongst us, he must at no very remote period, have established an imperishable name. As a public lecturer, and generally, in his didactic capacity, his language was clear and concise, his manner earnest and agreeable, his matter admirably arranged and carefully selected. He had, indeed, considering the short time in which he had been engaged in the difficult business of teaching Chemistry, acquired a singular command over the lecture table, much dexterity in the public performance of illustrative experiments, and in that methodical aptitude which ensures the attention of the hearer, by at once amusing and instructing him, and which makes obscure truths plain, and dry details attractive.

As an *original inquirer* he had, as I have before observed, already laid the foundation upon which a permanent and worthy superstructure would doubtless have been raised: to this his various contributions to Chemical Science, and more especially to Organic Chemistry, bear ample testimony. I would now especially allude to those researches in which he, for the first time, succeeded in the artificial production of a *vegeto-alkali*, or an *organic salt-base;* to his discovery of *Furfurole*, and of *Benzoline;* no one can peruse his papers upon these subjects, which he communicated to the Royal Society, and which have a place in the Philosophical Transactions for 1845, without finding ample justification of the view which I have taken of their importance, or admitting the just discrimination of that learned body, in conferring upon their author the well-deserved testimony of their high sense of his deserts, in presenting him with one of the Royal Medals.* Our own Memoirs and Journals are also enriched with his papers on the preparation of an Artificial Yeast, on the action of Oil of Vitriol on the Ferrocyanide of Potassium, on the preparation of Hippuric Acid, on the analysis of South-Sea Guano, on the analysis of organic substances containing Nitrogen, on the preparation of Ether, and on the presence of Phosphoric Acid in the Felspar of Jersey.

Of these, and other original papers published elsewhere, I would willingly have said much more, and it would have been a grateful task to me to have enlarged upon their individual merits; but I have already disposed of the time allotted to these matters; I must therefore conclude, with reminding you further, that Mr. Fownes was the author of an excellent Manual of Chemistry, of which the first edition was published in 1844, and of a third edition of which he had completed the corrections and additions only a few days previous to his death. He was also the author of "An Essay on Chemistry, as Exemplifying the Wisdom and Beneficence of God." This latter production obtained for him, at the hands of the Managers of the Royal Institution, the Septennial Actonian Prize of 100 guineas; that body being empowered, under certain conditions, to award the said prize to such person as shall, in their judgment, be the author of the best Essay, in such department of science as they may select, illustrative of the beneficence of the Almighty.

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* The Philosophical Transactions also contain two other of his papers presented to the Royal Society, namely, one on the existence of Phosphoric Acid in rocks of igneous origin (Phil. Trans., 1844), and another on the amount of absolute Alcohol in spirit of different specific gravities (Phil. Trans., 1847).

We have lost one other Member, namely, Mr. Thomas George Tilley. He associated himself with us at a very early period of the existence of our Society, and has the honour, I may now justly say, of having communicated the first paper which was read at our table (April 27, 1841), and which has a place in our published Memoirs. It relates to the products of the action of Nitric Acid on Castor Oil. One other paper we also have from Mr. Tilley, "On the conversion of Cane-Sugar into a substance isomeric with Cellulose and Inuline," printed in our Memoirs for 1845.

Mr. Tilley, who was born at Brentwood, in Essex, was not much resident amongst us, and I have only been able to collect a very few particulars respecting him. I believe that the foundation of his chemical education was laid at Edinburgh, under Dr. Christson, he then went to Paris, and afterwards studied at Berlin, and at Giessen, and was made a Ph.D. On his return to England, he published an Essay on Agricultural Chemistry, and others on the supposed conversion of Carbon into Silicon, and of Iron in Rhodium, and became, in 1845, Professor of Chemistry in Queen's College, Birmingham. About the same time, he published a paper on Bebeerine, in conjunction with Dr. Maclagan, in the Philosophical Magazine. He had not long been resident in this country when his health began to fail, and induced him to court the aid of change of air and scene; and after travelling for some time in various parts of Europe, he at length took up his abode at Prague. Here we find him working in Professor Redtenbacher's Laboratory, whence his last highly interesting paper on Œnanthol and its compounds, is dated, and which is published in the Philosophical Magazine for August, 1848. It deserves mention, as one amongst the abundant instances of the abominations of war, that whilst engaged in those investigations, the laboratory was ransacked, all that it contained destroyed, and Mr. Tilley narrowly escaped. Dr. Francis, to whom I owe these details, says in a letter to our Secretary, dated the 27th instant, that on his return from Prague to this country, he complained of the state of his lungs, and intimated his apprehension of being unable to sustain the vicissitudes of this climate; and it appears that shortly afterwards he repaired to Paris, and died in that city.

And now, allow me to add, that this memorandum of our deceased Members, necessarily reminds me of the loss which Science has sustained, in the course of the preceding year, by the death of Berzelius,—a name justly celebrated throughout the scientific world, and to whom Chemists especially owe a heavy debt of gratitude and of respect. It is true that his name was not specifically enrolled amongst those of our Members; but his high station, his pre-eminent talents, and his moral excellence, endeared him to us all; and I am sure you will join with me, in doing, what I may call filial homage, to his memory.

The labours of your Council, during the past year, have been unusually important, and have been directed to objects deeply involving the future condition of our Society.

At your last Annual Meeting, the Council announced their intention of publishing the Memoirs and proceedings of the Society in the form of a *Quarterly Journal*, with a view of promoting the more speedy and regular circulation of the communications made to the Society, amongst its Members; this resolution of the Council has now been carried into effect, and four Numbers of the Journal have made their appearance, comprising no less than forty-one papers and communications from Members of the Society.

These Journals also contain Abstracts and Notices of all the most important papers which have appeared in the course of the year in the several Foreign Journals, and an extensive alphabetical list of the Titles of Chemical papers to be found both in the British and Foreign Journals.

Among the original papers which have been presented to, and read before the Society, and which have a place in the Journals of our Transactions, there are some of an elaborate description, and of great intrinsic importance, and which involve difficult and intricate research; many which are practically valuable from the new methods of manipulation which they disclose; and many, in which new facts are recorded, tending to facilitate the future progress of research upon the several points which are discussed in them. The number of these different communications prevents our adverting more specifically to those which we consider most important, or making a selection from the new discoveries, and methods of investigation, which are set forth in them; but we are satisfied that the whole collection is not only eminently creditable to the individuals in whose labours they originate, but that they tend to the honour and repute of the Society, of whose Transactions they form a part.

The Library and Chemical Collection of the Society are making slow, but not unsatisfactory progress. In addition to the periodical publications purchased by the Society, the following presentations have been made to the Library, namely:—

"Memoirs of the Geological Survey of Great Britain, and Memoirs of the Museum of Economic Geology;" presented by the Museum.

"Report upon the Coals suited to the Steam Navy;" by Sir H. de la Beche and Dr. Lyon Playfair: from the authors.

"Papers on the Colouring Matter of Morinola Citrifolia, and on the Distinctive Distillation of Animal Substances;" by Thos. Anderson, M.D.: from the author.

"An Essay on the Comparative Value of the different kinds of Coal for the purposes of Illumination;" by A. Fyfe, M.D.: by the author.

"A paper on the Chemical Properties of Wax," from the Phil. Trans.; by B. C. Brodie, Esq.: by the author.

A paper "On the Phosphoric Strata of the Chalk Formation;" by Messrs. Payne and Way: by the authors.

"Report on the Analysis of the Ashes of Plants;" by Messrs. Way and Ogsden: by the authors.

"Transactions of the Society of the Friends of Natural Science in Vienna," and "A Collection of Papers upon Natural History;" by Dr. Haidinger.

"The American Journal of Science;" "The Journal of the Franklin Institute;" "The Pharmaceutical Journal:" by the Editors.

"A Calendar of the Meetings of Scientific Bodies for 1848-49;" by Mr. Taylor.

A lithographed portrait of Dr. Faraday, from a Daguerrotype; by M. Claudet.

The following articles have been presented to the Museum, namely:—

A specimen of the first piece of platinum consolidated from the spongy state, in England; and of the first piece of the same metal soldered with gold: by W. T. Cock, Esq.

A Balance-galvanometer: by Mr. W. S. Warde.

Specimens of Phosphate of Ammonia, and of Ammonio-phosphate of Soda: by Mr. J. T. Herapath.

Specimens of Phospho-cerite, and of the Oxides of Cerium, Lanthanum, and Didymium: by Mr. Watts.

The state of the funds of the Society will be evident, and I trust satisfactory, from the Treasurer's Audited Account, which is now lying upon your table.

And now, Gentlemen, having gone through the ordinary business which devolves upon the Chairman at this Meeting, it becomes my duty, before we proceed to ballot for a President and other Officers, to advert to the proceedings of a *Special Meeting* of the Society, which was held here on the 22nd of May last, at which Meeting your Council was duly authorized "to take the necessary steps for procuring a Charter of Incorporation, on the understanding that the expenses incurred by the funds of the Society should not exceed the sum of £400." I have now the pleasure of informing you, that this important and desirable object has been most satisfactorily attained, and that, under the excellent management and influence of the gentleman who solicited our Charter, the whole of the expenses incurred in reference to it amount to the sum of £330, towards which £132 have been subscribed by the Members.

The actual and prospective advantages thence accruing to the Society are various and important. We now take rank with the other *Chartered Scientific Societies;* and when we consider the zeal and energy which has already been displayed in promoting the views of this Society, and their important, popular, and universal character, for who can deny the vast importance of Chemical Science, both pure and applied, or where can we find a department of knowledge having more immediate bearings upon other sciences, upon manufactures, upon the common and fine arts, upon agriculture, upon medicine, in short, upon the luxuries, comforts and necessaries of life; when, I say, all these things are considered, we may surely reasonably hope and expect, that a Society aiming at the most dignified and useful objects, and embracing amongst its members many of the most celebrated Chemists of the World, will not only prosper, but that its resources will increase, and its dominion be extended, till it vies with any other Scientific Establishment of the country. I therefore thought that we, your Council, are especially bound to congratulate the Society upon the steps which we have been enabled to take towards increasing our stability, extending our usefulness, and strengthening our claims upon the support and respect of our scientific brethren, and of the public at large.

One other subject only suggests itself as requiring mention upon the present occasion, and it is one which, from time to time, has engaged the anxious attention of your Council, but which each succeeding Session renders more pressing, and at present calls for the speediest adjustment which is securely attainable. I mean, that having established our *name,* we should next think of a fit *local habitation,* and should endeavour to obtain possession not only of a meeting-room capable of affording us adequate and comfortable accommodation, but associated with a room for the reception of our books and chemical preparations, and also for the meetings of the Council. These desiderata are not easily attainable, but they will not be lost sight of by the Council.

You will now, Gentlemen, proceed to ballot for the Officers of the ensuing year, and the Secretary will then read the new Code of By-laws, which has been prepared by your Council in accordance with the provisions of the Charter of the Society. Of these By-laws there are printed copies upon the table; and we trust that they will now meet with your approval, and receive your sanction.

And now, Gentlemen, having completed the biennial period of my service as President, allow me, on resigning this Chair to my successor in that honorable office, most sincerely to thank you for the distinction which has been conferred upon me, and of which I shall always retain a grateful remembrance, together with an anxious desire to promote the welfare of the Society.

The following Gentlemen were elected Officers and Council for the ensuing year:

PRESIDENT.

Richard Phillips, Esq.

VICE-PRESIDENTS.

John Thomas Cooper, Esq.
Thomas Graham, Esq.
William Thomas Brande, Esq.
William Allen Miller, M.D.

SECRETARIES.

Robert Warington, Esq.
Edmund Ronalds, Ph.D.

FOREIGN SECRETARY.

A. W. Hofmann, Ph.D.

TREASURER.

Robert Porrett, Esq.

COUNCIL.

Thomas Andrews, M.D.
Bence Jones, M.D.
Walter Crum, Esq.
William Ferguson, Esq.
J. J. Griffin, Esq.
J. P. Joule, Esq.
Alfred White, Esq.
Lyon Playfair, Ph.D.
Edward Schunck, Ph.D.
S. Redwood, Esq.
E. F. Teschemacher, Esq.
Col. Ph. Yorke.

The thanks of the society were voted severally to the President, Secretaries, Officers and Council for their exertions during the past year.

The Charter of Incorporation and the Bye-Laws as revised by the Council to accord with the clauses of the Charter, were presented to the Society, and it was resolved:

That these Laws be adopted as the Bye-Laws of the Society.

Resolved:

That the thanks of the Society be given to Mr. Tooke, for his friendly services in soliciting the Charter of Incorporation.

The following audited Report of the Treasurer was submitted to the Society, and the Society then adjourned to April 2nd.

AUDITED REPORT OF THE TREASURER.

Dr. ROBERT PORRETT (TREASURER) IN ACCOUNT WITH THE CHEMICAL SOCIETY OF LONDON. *Cr.*

		£.	s.	d.
1848. March 30.	To Balance from last Account	69	16	3
1849. March 30.	„ Subscriptions and Composition since received	351	0	0
„ „	„ Proceeds from sale of £150, 3 per cent. Consols.	134	1	3
„ „	„ Donations from sundry Members towards the expenses of the Charter	99	13	0
„ „	„ Proceeds from sale of "Memoirs," &c.	5	16	0
„ „	„ Dividend, ½ year to 10th Oct. last, on £400, 3 per cent. Consols.	5	16	6
	£	666	3	0

		£.	s.	d.
1849. March 30.	By payment to Mr. Tooke for Charter Expenses	300	0	0
„ „	By Ditto to H. Baillière, Publisher, for the "Journal," £113 6*s.* 2*d.*, and for Books, £12 7*s.* 6*d.*	125	13	8
„ „	By Ditto to D. Nutt, for Books	1	5	0
„ „	By Ditto to Rd. & I. E. Taylor, for Printing "Memoirs"	60	12	2
„ „	By Ditto to the Editor of the "Journal," and for Postage	58	4	4
„ „	By Ditto of Rent to the Society of Arts	25	0	0
„ „	By Ditto of Poundage to the Collector, and for Printing Cards, Postage, &c.	20	9	9
„ „	By Ditto for Tea, Coffee, Servants, &c.	5	8	9
„ „	By Ditto for Stationery and Stamps for Treasurer and Secretary	2	7	0
„ „	By Balance carried to new Account	67	2	4
	£	666	3	0

London, March 30, 1849.

R. Porrett, Treasurer.

We have examined the above Account, and find it correct.

Jacob Bell.
Charles Button. } Auditors.

[To face page 192.

THE
QUARTERLY JOURNAL
OF THE
CHEMICAL SOCIETY OF LONDON.

April 2, 1849.

The President in the Chair.

Mr. George Phillips presented to the Society a bottle enclosing a curious film of gun-cotton, which had been formed inside the phial by the spontaneous evaporation of the ether from a collodion solution.

The following paper was read:

XVIII.—*Analysis of Gold-dust from the Coast of California.*

By E. T. Teschemacher, Esq.

The great interest excited by the recent discovery of large quantities of gold-dust existing in the sand in the district of California, has induced me to lay before the Chemical Society the results of some examinations I have lately made with reference to its composition. The specimen of gold analysed was received from my brother, resident in Boston, United States. An analysis of Californian gold has likewise been made by Mr. T. H. Henry, and published in the Philosophical Magazine for the present month. I think it desirable that a number of such analyses should be made and registered, in order that an opinion may be formed upon the greater or lesser uniformity in composition of the gold from different parts of the same district; and although I am unacquainted with the exact locality of my specimen, still, as the more immediate sources from which the two specimens were derived were so different, it is not at all likely that the locality in which they were found was the same.

My specimen was in the state of flattened grains, weighing from ¼ of a grain to 5½ grains each; the grains were roughened on the surface, and of a dull brass-yellow colour, and were partially encrusted by many black specks and some brilliant crystals of magnetic iron, with a portion of sand embedded in the cavities. The specific gravity of the dust was 16·33.

The quantity submitted to analysis was 15 grains. It was first boiled in hydrochloric acid, and after well washing, was boiled in dilute nitric acid. The hydrochloric acid dissolved the exterior black specks and the crystals of oxide of iron. The solution obtained was precipitated by ammonia, nothing having been dissolved but peroxide of iron, weighing 0·07 grains. The subsequent treatment with nitric acid was tried in order to ascertain whether any silver would be dissolved out; but no action whatever took place. The separate action of these acids rendered the grains of gold of a brilliant gold colour. The gold-dust was then acted upon by aqua-regia. The gold was dissolved, leaving the silver in the state of an insoluble chloride. The chloride of silver was dissolved in ammonia, and having been evaporated from the sand, was reprecipitated by nitric acid. It weighed 1·36 grains. The sand weighed 0·10 grains.

The solution of gold was evaporated to dryness and hydrochloric acid added to it; the gold was then precipitated by oxalic acid in excess, and after digestion for three days, was separated; it weighed 13·45 grains. Sulphuretted hydrogen was passed through the solution, after the separation of the gold, a small precipitate was produced, which I expected to be sulphuret of copper; but upon dissolving it in a small quantity of nitric acid, and adding ammonia, not the slightest indication of copper appeared; on further examination, it proved to be gold, which had escaped precipitation by the oxalic acid; it weighed 0·10 grains. The solution was now evaporated to dryness; re-dissolved in hydrochloric acid and precipitated by ammonia, the precipitate weighed 0·08 grains, and consisted of peroxide of iron.

The composition is, therefore, as follows:

13·55 gold	or in 100	parts	90·33 gold
1·02 silver	,,	,,	6·80 silver
0·15 oxide of iron	,,	,,	1·00 oxide of iron
0·10 sand	,,	,,	0·66 sand
14·82			98·89

Deducting the oxide of iron and the sand, the alloy would consist of:

92 parts of gold
7 ,, silver

99 parts

The gold-dust analysed by Mr. Henry, had a spec. grav. of 15·96, and consisted of

Gold	88·75
Silver	8·88
Copper with a trace of iron	0·85
Siliceous matter	1·40
	99·88

Or deducting the siliceous matter,

Gold	90·01
Silver	9·01
Copper	0·86
	99·88

shewing thus a difference of about two per cent in the silver contained in the two specimens of Californian gold.

Another portion of the same sample which I examined, contained about eight per cent of silver.

April 16, 1849.

The President in the Chair.

Messrs. J. Bailey and T. M. Creggan were elected Fellows of the Society.

The following papers were read :

XIX.—*Analysis of the Thames Water at Greenwich.*

By Edward T. Bennett.

STUDENT IN THE ROYAL COLLEGE OF CHEMISTRY.

In pursuing the series of investigations of the water of the Thames at different localities, suggested by Dr. Hofmann, two of which, the one of the water as it is found at Twickenham, by G. F. Clark, and the other at London Bridge, by J. M. Ashley, are before the Chemical Society, we have at his request, and under his direction and assistance, undertaken a third analysis, for which the water was collected at Greenwich, after having been subjected to the influences, both of the London drains, and of the sea water coming up with the tide. The water was taken from the middle of the river, exactly opposite the Hospital, just after the turn of the tide, on the 1st of January, 1849. It was full moon on the 8th instant at 10h. 50m. P.M., and was therefore nearly the highest spring tide; but the wind was blowing very strongly direct down the river, which had a material effect in keeping back the sea water, on that particular day. The following observations were made at the time.

Temperature of the water	3^{0} C. ($37·4^{0}$ Fahr.)
Temperature of the air	9^{0} C. ($48·2^{0}$ Fahr.)

The reaction of the water was very slightly acid. It had no perceptible taste or odour.

The specific gravity of the water, after everything held in mechanical suspension had completely subsided, was 1·00116.

For the qualitative analysis, 42 imperial pints, equal to 23840 grammes, were evaporated to a concentration which yielded a precipitate, weighing, when dry, 5·5025 grammes; and a filtrate, with washings, of 364 grammes. The filtrate was of the colour of brown sherry, and strongly acid. The precipitate, on examination, indicated the presence of potash, soda, lime, phosphate of alumina, iron, silicic, carbonic, sulphuric, and hydrochloric acids, with organic matter. The only additional ingredient found in the filtrate was magnesia. Bromine and iodine could not be detected. Doubtful traces of nitric acid were observed, on highly concentrating a separate quantity of the water. On carefully evaporating 500 grammes of the water to dryness, and treating with lime, ammonia could not be discovered.

The quantitative analysis yielded the following results:

A. Determination of the total amount of fixed constituents.

	Amount of water employed.	Amount of residue obtained.	Per-centage in the water.
I.	780·975 grms.	0·3055 grm.	0·0391177
II.	1001·530 „	0·3910 „	0·0390402
III.	1000·000 „	0·4180 „	0·0418000
		Mean	0·0399859

B. Determination of sulphuric acid.

	Water employed.	Sulphate of baryta.	Per-centage of sulphuric acid.
I.	644·465 grms.	0·0913 grm.	0·0048722
II.	749·240 „	0·1008 „	0·0046180
III.	658·270 „	0·0808 „	0·0042089
		Mean	0·0045664

C. Determination of hydrochloric acid.

	Water employed.	Chloride of silver.	Per-centage of hydrochloric acid.
I.	523·010 grms.	0·062 grm.	0·0030158
II.	538·410 „	0·056 „	0·0026735
III.	615·530 „	0·064 „	0·0026673
		Mean	0·0027855

D. Determination of silicic acid.

Water employed.	Silicic acid.	Per-centage of silicic acid.
I. 853·695 grms.	0·0080 grm.	0·0012065
II. 1201·495 „	0·0133 „	0·0011069
III. 1200·215 „	0·0131 „	0·0010915
		Mean 0·0011349

E. Determination of lime.

Water employed.	Carbonate of lime.	Per-centage of lime.
I. 853·695 grms.	0·1905 grm.	0·0124974
II. 1201·495 „	0·2738 „	0·0127624
III. 1200·215 „	0·2733 „	0·0127517
		Mean 0·0126705

F. Determination of magnesia.

Water employed.	Pyrophosphate of magnesia.	Per-centage of magnesia.
I. 853·695 grms.	0·0278 grm.	0·0011602
II. 1201·495 „	0·0285 „	0·0008647
III. 1200·215 „	0·0290 „	0·0008812
		Mean 0·0009687

G. Determination of the alkalies.

Water employed.	Mixed chlorides.
I. 1668·840 grms.	0·1100 grm.
II. 1508·450 „	0·1021 „
III. 1000·000 „	0·0580 „

a. Estimation of potash.

Bichloride of platinum and potassium.	Per-centage of potash.
I. 0·0988 grms.	0·0011391
II. 0·0978 „	0·0010521
III. 0·0508 „	0·0009778
	Mean 0·0010563

b. Estimation of soda.

Chloride of sodium.	Per-centage of soda.
I. 0·0798 grm.	0·0025347
II. 0·0723 „	0·0025372
III. 0·0425 „	0·0022511
	Mean 0·0024410

H. Estimation of organic matter.

This was not attempted as soluble and insoluble matter in the filtrate and precipitate separately, which were obtained by evaporating a large quantity of the water, because the proportions thus determined must evidently have depended upon the degree to which the concentration had been carried. But for this purpose specific quantities of the water were evaporated to dryness, and the whole organic matter was burnt off, at the lowest effective temperature, with the aid of a current of oxygen.

Water employed.	Organic matter burnt off.	Per-centage of organic matter.
I. 1000 grms.	0·0515 grm.	0·00515
II. 1000 „	0·0611 „	0·00611
III. 500 „	0·0310 „	0·00620
		Mean 0·00582

I. Determination of carbonic acid.

At the time of collecting the water, a syphon capable of containing 534 cubic centimetres was filled three times, and discharged into each of four Winchester quart bottles, containing a mixture of chloride of calcium and ammonia. After complete subsidence, the precipitates which had formed, in two of the bottles,

together weighed . .	2·111 grms.
From the other two bottles „ . .	2·104 „
Total . . .	4·215 „

The carbonic acid was expelled by means of hydrochloric acid, in the usual apparatus.

Precipitate employed.	Carbonic acid evolved.	Per-centage in the precipitate.	Per-centage in the water.
I. 0·614 grm.	0·220 grm.	35·830	0·0235407
II. 0·465 „	0·163 „	35·054	0·0230309
III. 0·444 „	0·153 „	34·459	0·0226399
		Mean . .	0·0230705

The water from four other bottles was treated on the spot with a solution of arsenious acid in hydrochloric acid. The whole of the sediment, after standing some time, was collected on one filter, and carefully examined for sulphide of arsenic, but without success; thus proving the absence of free hydrosulphuric acid.

The indications of iron, in the form of soluble salts, were exceedingly slight. An attempt to estimate the phosphate of alumina gave 0·0003439 per cent; a quantity too minute for the separate determination of the phosphoric acid. Alumina was not found in any other state than that of phosphate.

Following the usual arrangement, by combining the whole of the acids and bases according to their chemical affinities, the ingredients found in the water, assume the subjoined form.

	In 100 litres Grammes.	In an imperial gallon Grains.
Sulphate of potash	1·9552	1·3710
Sulphate of soda	5·5937	3·9224
Sulphate of magnesia	0·7808	0·5475
Chloride of magnesium	1·6374	1·1482
Chloride of calcium	2·3205	1·6272
Carbonate of lime	20·5353	14·3997
Silicic acid	1·1349	0·7958
Phosphate of alumina Iron	traces.	traces.
Organic matter	5·8200	4·0810
	39·7778	27·8928
Direct determination of fixed constituents	39·9859	28·0387

Deducting from the total per-centage of carbonic acid the portion in combination with lime, the per-centage of free carbonic acid amounts to 0·014035; corresponding to 7161·813 cubic centimetres in 100 litres, or to 19·8535 cubic inches in an imperial gallon.

The arrangement as above does not exhibit any chloride of sodium in the water, which no doubt must exist, as such, in the Thames at Greenwich, especially at high water. In the same manner sulphate of lime is undoubtedly present, though not shown in the table. But as the precise form or the proportions in which the individual constituents are distributed in a mixed solution is not known—for experiment proves they may be variously associated in solution according to the degree of concentration—every arrangement must be more or less hypothetical. We have therefore adopted the principle followed in the preceding analyses of combining the strongest acid with the strongest base as affording the best means of comparison.

The general features of the foregoing analysis exhibit a large increase in the amount of the fixed constituents as compared with the water taken at Twickenham, but not as compared with that from London Bridge. This appears intelligible from a portion of the large amount of organic matter, found at London Bridge, having disappeared in the further course of the river. The total amount of fixed constituents being, however, but slightly diminished, the rather considerable decrease of organic matter must be supplied by something that the water has taken up. We find this to consist principally of the alkalies, magnesia and carbonate of lime, the latter being taken up and held in solution by carbonic acid. In looking for a source of the additional amount of carbonic acid, we think it may be found in the decomposition of the various organic matters, both soluble and insoluble, which are daily carried into the Thames, and of which, as our analysis shows, a portion disappears in the progress of the river from London Bridge to Greenwich; although this diminution may have been partly occasioned by the influx of sea-water. By comparing the different results of the several analyses, it becomes evident likewise, that the waters of the river are affected by other local circumstances, probably at both these stations. It may be mentioned that there are several chemical works which pour their refuse into the river, both above and below the point where the water which is the subject of the present analysis was taken.

I cannot conclude this paper without mentioning that I have been kindly assisted in this analysis by my father and brother, so that each determination is the result of at least three separate and independant experiments.

XX.—*Analysis of a Medicinal Water from the Neighbourhood of Bristol.* *By* THORNTON J. HERAPATH, ESQ.

At a distance of about fifteen miles from Bristol, on the Cherry Rock Farm,* in the parish of Kingswood, Gloucestershire, there exists a spring or well of water, which has been long held in great estimation by the inhabitants of Kingswood and the surrounding districts, on account of its highly medicinal qualities. According to the present proprietor, Mr. W. A. Long, of Wotten-under-Edge, (at whose request it was that the following analysis was undertaken), the water was analysed about forty years ago, and a pamphlet written upon the subject; but nothing can be now learnt with regard to the name of the analyst, or the results of his examination. It appears from the information which has been kindly afforded me by the above-mentioned gentleman, that the well from which the water was obtained is from 45 to 50 feet in depth, and the water rises to within 24 or 25 feet of the surface; its quantity is never sensibly affected either by a wet or dry season. The surface is a thin mould, which rests upon a stratum of stiff clay of about five feet in depth; this clay is stained with iron in several places. This is succeeded by a bed of blue lias stone, which contains numerous fossil shells.* There are several thin beds of this stone, and in the spaces between them is stiff clay strongly impregnated with salt, which can be seen glistening in it as well as tasted. Below this again, there is, for about 15 feet, a dry marly clay, which is described as being much mixed with the above-mentioned fossil-shells, and round smooth stones like lap-stones. It is from the bottom of this bed that the water rises.

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* This farm is now in the occupation of Mr. T. Alway, and is distant about three-quarters of a mile from the town of Wickwar; half a mile from the Wickwar station; one mile from the village of Kingswood, and three miles from the Charfield station on the Bristol and Birmingham Railway.

Most of the springs in this neighbourhood, when sunk to a great depth, are generally inclined to be salt, and a great deal of the blue lias stone, which is plentifully met with here, is stained with iron.

The temperature of the water, when taken, differed only by about one degree from that of the surrounding atmosphere. Its specific gravity at 60° Fahr. was 1·00507. It evinced a slightly acid reaction with very delicate test-paper; this, however, was most probably caused by the free carbonic acid present in the water, as the paper immediately resumed its original colour upon the application of a gentle heat. The water possessed a very marked, unpleasant, saline taste. It was neither chalybeate nor sulphureous; but the rapid manner in which it underwent decomposition, upon keeping, showed that it contained a large proportion of organic matter.†

A qualitative analysis likewise pointed out the presence of sulphuric, carbonic, crenic and apocrenic acids, chlorine, lime, magnesia, soda and potash. There were also small quantities of phosphoric and nitric acids, iodine, bromine (?), oxide of iron, silica and alumina (?).

Quantitative analysis.

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* Described by the well-diggers as greatly resembling cockle-shells.

† This was still more clearly shown by its behaviour with chloride of gold, when tested in the manner recently proposed by M. A. Dupasquier (Journ. de Pharm. et de Chim. XIII. 164; also Comptes Rendus, Avril 5, 1847). Upon adding a few drops of a solution of this salt to two or three hundred grains of the water contained in a small flask, and applying heat, as soon as the liquid began to boil, the brownish-red tint, mentioned by that chemist, became immediately perceptible. The same effect was produced by exposing the solution to the sun's light, but more slowly.

A. Determination of the total amount of saline constituents.

	Water employed.	Weight of fixed residue.	Per pint.
I.	8794·36250 grs.	56·200 grs.	56·200
II.	4397·18125 „	28·156 „	56·312
		Mean.	56·256

B. An imperial pint (8794·3625 grs.) of the water was boiled for one or two hours in a porcelain vessel, until all traces of the carbonic acid were expelled, it was then allowed to remain undisturbed for some hours, in order to give time for the precipitated carbonates, &c. to deposit; the supernatant fluid having been drawn off by a syphon, the precipitate was collected on a filter, well washed with water, dried at about 300 or 350° F. and weighed; it amounted to 3·85 grains in weight, (*a*).

As it was found that a small quantity of the earthy carbonates still obstinately adhered to the sides of the basin, it was dissolved off by means of a few drops of dilute hydrochloric acid; the acid solution thus obtained was supersaturated by a little carbonate of ammonia, and evaporated to dryness; the residue, having been gently ignited to expel the ammoniacal salts, was found to weigh 0·26 gr. This was added to the carbonates previously obtained (*a*), and both were subjected to analysis. They gave of

Carbonic acid . .	1·747 grs			
Carbonate of lime.	3·978 „	=	Lime. . .	2·22770 grs.
Sulphate of barytes	0·034 „	=	Sulphuric acid	0·01150 „
Silica*	0·120 „			

These numbers are equivalent to

Carbonate of lime . . .	3·96665
Sulphate of lime . . .	0·01955
Silica	0·12000
	4·10620

Besides the above, I also detected exceedingly minute traces of oxide of iron, alumina, magnesia, and phosphoric acid; but they were much too small in quantity to be estimated with exactness.

C. The filtered water, having been intimately mixed with the washings of the filter (*a*), was carefully divided, by means of a graduated tube, into four separate portions of equal weight. Of these, the first, was employed for the estimation of the sulphuric acid and chlorine; the second, for that of the lime and magnesia; in the third, the soda and potash were estimated; and in the last, the organic matter.

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* This residue of silica was dark in colour, but, upon being heated to redness, became perfectly white, although it did not experience any perceptible diminution in weight. This would appear to prove the presence of a little bituminous matter.

The following quantities were obtained:

Sulphate of barytes 18·328 grs. = sulphuric acid 6·2124 grs. =24.8496 per pint;

Chloride of silver (fused)* 4·657 grs.=chlorine 1·16425 grs. =4·657 per pint.

The second portion gave:

Carbonate of lime 1·725 grs.=lime 0·9658 grs.=3.8632 grs. per pint:

Pyrophosphate of magnesia 3·837 grs.=magnesia 1·3704 grs. =5·4816 grs. per pint.

The third portion gave:

Mixed alkaline chlorides 5·125 grs.:

Potassio-chloride of platinum 0·086 gr. = chloride of potassium 0·0262 gr. = potash 0·0165 gr. = 0·0660 per pint; there were therefore of

Chloride of sodium 5.0988 grs.=2·7193 grs. of soda=10·8772 per pint.

The fourth portion was evaporated to dryness at about 300° to 320° F., and the residue was kept at that temperature until its weight remained constant; it was then heated to redness with an excess of anhydrous carbonate of soda, and the loss of weight noted; it amounted to 0·826 grs.; consequently the entire weight of the organic matter contained in a pint of water was 3·304 grs.†

D. Estimation of the iodine.—The alcoholic solution of the salts contained in a quart of the water was evaporated to dryness, the residue re-dissolved in a small quantity of water, and the solution, precipitated by proto-chloride of palladium; the iodide of palladium obtained, when dried at 212° F., was found to weigh 0·022 gr. = 0·0154 gr. of iodine = 0·0077 gr. per pint = 0·0143 gr. of iodide of silver.

F. Estimation of the nitric acid.—The salts which remained after the evaporation of 17588·725 grains of the water, were introduced into a small tube-retort, where they were treated with a slight excess of moderately-strong sulphuric acid. The mixture was then heated in a sand-bath, and the acid vapours, which were given off, were conducted into a glass receiver, where a large excess of recently precipitated carbonate of silver was held in suspension in a small quantity of distilled water. Great care was taken to suspend the operation immediately upon the appearance of the fumes of sulphuric acid. The solution of nitrate of silver, &c., which remained in the receiver, having been boiled to expel any carbonic acid which might have been present, was filtered to separate the excess of carbonate and chloride of silver, and precipitated by a little dilute hydrochloric acid; the chloride of silver thus produced (which of course corresponded to the nitrate of silver present in the solution) was collected on a filter, washed, &c., and weighed: Ag Cl (fused) = 0·038 gr. = nitric acid 0·014 gr. = 0·007 per pint.*

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* The reduction, which subsequent experiment proved it was necessary to make in this, on account of the presence of iodide of silver, indicated the true quantity of chloride of silver to be 4·6534 grs.=chlorine 1·16335 grs=4·6534 grs. per pint.

† For the estimation of the crenic and apocrenic acids, *see F.*

G. Estimation of the Organic Acids.—The whole of the salts which remained upon the evaporation of a quart of the water, were boiled for a short time with a dilute solution of potash. The solution having been filtered, and the excess of alkali supersaturated with acetic acid, it was precipitated by acetate of copper, &c., in the usual manner. It gave of

Aprocrenate of copper† 0·458 gr. = apocrenic acid 0·3538 gr. = 0·1769 per pint.

Crenate of copper 0·3510 gr. = crenic acid 0·2562 gr. = 0·1281 per pint.

If we deduct, therefore, from the entire weight of the organic matter obtained by the preceding experiments, = 3·3040 grs., that of the above described organic acids 0·3050 gr. (0·1796 + 0·1281), we obtain 2·9990 grs. as the true weight of the extractive or nitrogenous organic matters contained in a pint measure of water.

G. Estimation of the gaseous carbonic acid.—This was performed in the usual manner, by passing the gas which was evolved upon boiling the water through an ammoniacal solution of chloride of calcium. A pint measure of the water gave 4·43 grs. of carbonate of lime = 1.9492 grs. of carbonic acid = 4·1242 C.I. at the ordinary temperature and pressure.‡

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* For this simple and elegant method of estimating the nitric acid, I am indebted to my father, Professor W. Herapath, by whom it has been long known and adopted.

† In the above calculations, the numbers given by Berzelius for the atomic weights of the two acids have been employed. According to his experiments, the combining equivalent of apocrenic acid would appear to be represented by the number 135·6, and that of crenic acid by 108·0.—Poggendorff's Annalen, xxix, 238 et seq.

‡ 100 C.I. weigh 47·262 grs.—Dulong and Berzelius.

From the analytical results contained in the preceding pages, the following composition for this mineral water has been deduced:

Per pint = 8794·3625 grs. Per gallon = 70357·9 grs.
Carb. acid gas, at 60° F. 4·1242 C.I. = „ 32·9936 C.I.

	Imperial pint.	Imperial gallon.
Fixed constituents.		
Chloride of magnesium	0·0600	0·4800 grs.
Chloride of potassium	0·1048	0·8384
Chloride of sodium	7·6030	60·8240
Iodide of sodium	0·0090	0·0720
Bromide of sodium ?	traces.	traces.
Sulphate of magnesia	16·2190	129·7520
Sulphate of soda	15·3450	122·7600
Sulphate of lime	9·3895	75·1160
Nitrate of lime	0·0120	0·0960
Apocrenate of magnesia	0·2030	1·6240
Crenate of magnesia	0·1450	1·1600
Nitrogenous organic matter	2·9990	23·9920
Carbonate of lime	3·9666	31·7328
Carbonate of magnesia	traces.	traces.
Carbonate of protoxide of iron	traces.	traces.
Phosphate of lime	traces.	traces.
Alumina ?	traces.	traces.
Silica	0·1200	0·9600
Bituminous matter ?	traces.	traces.
	56·1759	449·4072
Absolute quantity of saline ingredients obtained	56·2560	450·0480

May 7, 1849.

The President in the Chair.

The address delivered at the Anniversary Meeting of the Geological Society, by Sir Henry de la Beche, was presented by the author.

The following communication by Mr. Danson was read; likewise a note on a singular substance resulting from Cloves, by Dr. R. Scott, of Liverpool, and a note on the composition of the Deep Well Water of the Royal Mint, by W. T. Brande, Esq.*

XXI.—*On the Sulphites of Potash, Chromium, Lithia and Bismuth.*

By Joseph Danson.

STUDENT IN THE LIVERPOOL COLLEGE OF CHEMISTRY.

In Dr. Muspratt's † paper on the sulphites, the composition of the above-mentioned salts was not ascertained; I therefore undertook their preparation and analysis, with a view of lessening the gaps in this interesting series.

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* The publication of this paper has been deferred at the request of the author.

† Liebig's Annalen, Band L. 1844, page 259.

Sulphite of potash.—This salt was obtained by passing sulphurous acid through an aqueous solution of potash until the liquid smelt strongly of the gas; ether was then added to the solution, which was placed in a flask, well corked, and allowed to stand at rest for three weeks—during this time a white crystalline precipitate was deposited.

0·2040 grm. gave 0·2729 grm. sulphate of baryta = 0·0746 sulphurous acid, or 36·56 per cent.

0·1204 grm. gave 0·1600 grm. sulphate of baryta = 0·0437 sulphurous acid, or 36·29 per cent. Centesimally represented:

		Theory.	Found.		Mean.
			I.	II.	
1 equiv. of Potash . . .	48	53·93	—	—	—
1 „ „ Sulphurous acid	32	35·95	36·56	36·29	36·42
1 „ „ Water. . . .	9	10·11	—	—	—
	89	99·99			

Formula $KO\ SO_2 + aq.$

I can only account for the excess in the sulphurous acid from the presence of traces of sulphuric acid in the salt. It has been remarked that a *sulphite* can scarcely be kept for an hour exposed to the air, without a portion being converted into *sulphate;* in this respect the salts of sulphurous acid differ from those of selenious acid, which do not oxidize on exposure.*

Sulphite of Chromium.—This salt is formed by passing sulphurous acid through water, holding in suspension freshly precipitated oxide of chromium; when the gas was passed through the menstruum for some time, the whole becomes clear, forming a dark green liquid. If the solution be now boiled to expel the excess of acid, a green powder is deposited, having the following composition:

$$2\ Cr_2\ O_3\ 3\ SO_2 + 16\ aq, \text{ or } 2\ (Cr_2\ O_3\ SO_2) + HO\ SO_2 + 15\ aq.$$

I expected to find the chromium salt correspond with the sulphites of alumina and sesquioxide of iron, but the analytical results at once destroyed the supposed analogy. The following formulæ represent the three compounds:

Sulphite of alumina . . . $Al_2\ O_3\ \ SO_2 + 4\ aq.$
Sesquisulphite of iron . . . $Fe_2\ O_3\ \ SO_2 + 7\ aq.$
Sulphite of chromium : . $2Cr_2\ O_3\ 3SO_2 = 16\ aq.$

The analysis of the salt yielded the following results:

0·1020 grm. gave, when heated to redness, 0·0408 grm. of the oxide of chromium, or 40·00 per cent.

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* On the salts of selenious acid, Quart. Journ. of Chem. Society, April 1, 1849, page 54.

0·1467 grm. gave 0·1280 grm. sulphate of baryta=0·0350 sulphurous acid, or 23·85 per cent. Centesimally represented:

	Theory.		Found.
1 equiv. of Oxide of chromium . .	160	40·00	40·00
3 ,, ,, Sulphurous acid . . .	96	24·00	23·85
16 ,, ,, Water	144	36·00	—
	400	100·00	

When heated in a test tube, moisture and sulphurous acid are given off; when the heat is continued for some time, a mirror forms on the upper part of the tube, disappearing when the heat is increased.

Sulphite of Lithia.—If sulphurous acid be passed through water, holding in suspension the carbonate of lithia, the whole soon dissolves, forming a colourless liquid; the salt may be procured either by adding absolute alcohol, or by boiling the solution to expel the free acid, when white feathery crystals are deposited, which, on exposure to the atmosphere, become of a light yellow colour.

0·0563 grm. gave 0·0663 grm. sulphate of baryta = 0·01821 sulphurous acid, or 32·14 per cent. Centesimally represented:

	Theory.		Found.
1 equiv. of Lithia	14	14·00	—
1 ,, ,, Sulphurous acid . .	32	32·00	32·14
6 ,, ,, Water	54	54·00	—
	100	100·00	

Formula $LiO\ SO_2 + 6\ aq$.

Sulphite of Bismuth.—I obtained this salt by agitating freshly precipitated oxide of bismuth with a strong solution of sulphurous acid, keeping the mixture in a flask well corked for four days; the precipitate was of a straw colour, but became nearly white when dry. Heated in a test tube, the salt sublimed, giving off no moisture.

0·1810 grm. gave 0·1593 grm. oxide of bismuth, or 81·01 per cent. centesimally represented:

	Theory.		Found.
1 equiv. of Oxide of bismuth .	237	88·10	88·01
1 ,, ,, Sulphurous acid . .	32	11·89	—
	269	99·99	

Formula $BiO_3\ SO_2$.

The oxide of bismuth obtained by heating the nitrate to redness, does not absorb *any* sulphurous acid.

This sulphite, in all probability, corresponds with the carbonate $BiO_3\ CO_2$?

May 21, 1849.

Wm. Allen Miller, M.D., Vice-President, in the Chair.

William Glass, Esq., was elected a Fellow of the Society.

The following papers were read:

XXII.—*An Analysis of Plate Glass.*

By Messrs. J. E. Mayer and J. S. Brazier,

STUDENTS IN THE ROYAL COLLEGE OF CHEMISTRY.

In going over the analyses of the different varieties of glass which have been recorded, we find that but little attention has been paid to the composition of plate glass, a material which is almost becoming a necessary of life. It is, moreover, remarkable, that no analysis of the plate glass manufactured in Great Britain, has ever been published. The following pages contain the results obtained from the analysis of three different specimens of plate glass, which we undertook at the request of Dr. Hofmann.* These specimens were procured at the three most extensive plate glass manufactories of England.

Which are—

I. The British Plate Glass Company, St. Helens, Liverpool.
II. The London Thames Plate Glass Company, Bow Creek, Blackwall.
III. The London and Manchester Plate Glass Company, Sutton St. Helens, Liverpool.

For the purpose of analysis, these specimens of glass were reduced to the most minute state of division, which was effected by levigating in the usual manner. None of the specimens, whilst digesting in water, gave any reaction with the most delicate test papers.

To determine the extent of their solubility in water, from four to five grammes were digested in that menstruum for about forty-eight hours, the clear solution, in each case, yielded on evaporation but a slight residue, too small for determination.

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* I am indebted for these specimens to the kindness of Mr. Fincham of the British Plate Glass Works.—*Dr. A. W. Hofmann.*

The specific gravity of these specimens of glass is as follows:

British Plate Glass	2·319
London Thames Plate Glass	2·242
London and Manchester Plate Glass . .	2·408

A qualitative examination showed the presence of silicic acid, potash, soda, sesquioxide of iron, alumina, lime, and in one case traces of manganese.

The silicic acid was determined in the usual manner, by fusion with pure carbonate of potash. The sesquioxide of iron, the alumina, and the lime, were afterwards precipitated from the hydrochloric filtrate.

To determine the alkalies, the glasses were decomposed by means of hydrofluoric acid, in an apparatus recommended by Brunner,* which consists of a leaden capsula with a flat bottom about six inches in diameter and four inches high, in the centre of which is placed a small leaden ring about an inch and a half high, which serves as a support for a platinum dish. The leaden capsula has a cover fitting perfectly tight.

To set the apparatus in action, it is necessary to cover the bottom of the capsula with a layer of pulverized fluorspar about half an inch in thickness, and to pour upon it some sulphuric acid, sufficient to form a thick paste. A weighed portion of the finely powdered glass, after being put in the platinum dish, is covered with water, and placed on the leaden ring. The whole is then kept at a gentle heat either on a sand bath, or by means of a spirit-lamp.

By a few preliminary experiments, we found the action on the glass to be exceedingly slow, when covered merely with water; it was then suggested to us by Dr. Hofmann to try, instead of water, a strong solution of ammonia; we found that, the hydrofluoric acid being much more rapidly absorbed by this latter agent, the decomposition was facilitated in a remarkable manner.

The first of the two following tables shows the amount of substance employed; the results obtained are exhibited in Table II.

TABLE I.

	I. British Plate Glass.		II. London Thames Plate Glass.		III. London & Manchester Plate Glass.	
	1	2	1	2	1	2
	grm.	grm.	grm.	grm.	grm.	grm.
Quantity of glass for general analysis . .	1·3429	1·1750	1·1579	1·1906	1·0508	1·1095
Quantity of glass for estimation of alkalies	1·9400	2·1500	1·4200	1·6800	1·0200	2·0700

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* Poggendorff's Annalen, xliv. page 134.

TABLE II.

	I. British Plate Glass.		II. London Thames Plate Glass.		III. London & Manchester Plate Glass.	
	1	2	1	2	1	2
	grm.	grm.	grm.	grm.	grm.	grm.
Silicic acid	1·0402	0·9180	0·9090	0·9390	0·8200	0·8630
Chlorides of potassium and sodium . . .	0·5700	0·6460	..	..	0·2675	0·5360
Bichloride of platinum and potassium . .	0·3100	0·3610	..	..	0·0925	0·1835
Chloride of sodium .	0·4735	0·5360	..	..	0·2390	0·4790
Sesquioxide of iron and alumina	0·0127	0·0105	0·0320	0·0495	0·0373	0·0405
Carbonate of lime . .	0·1266	0·1135	0·1245	0·1305	0.0887	0·0987
Sulphates of potash and soda	..	..	0·4105	0·4940	..	..
Sulphate of baryta. .	..	..	0·6645*	0·7960*	..	..

The following numbers correspond with the foregoing results:

I.—BRITISH PLATE GLASS.

	I.	II.	MEAN.
Silicic acid	77·4592	77·2700	77·3646
Potash	2·8110	3·2192	3·0151
Soda	12·9232	13·2028	13·0630
Lime	5·2192	5·4096	5·3144
Manganese	,,	,,	,,
Sesquioxide of iron . .	0·9457	0·8936	0·9197
Alumina	trace	trace	trace
	99·3583	99·9952	99·6768

II.—LONDON THAMES PLATE GLASS.

	I.	II.	MEAN.
Silicic acid	78·5050	78·8669	78·6859
Potash	1·2744	1·4176	1·3460
Soda	11·5919	11·6724	11·6322
Lime	6·0605	6·1380	6·0992
Manganese	,,	,,	,,
Sesquioxide of iron . .	trace	trace	trace
Alumina	2·7636	2·5970	2·6803
	100·1954	100·6919	100·4436

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* These numbers were obtained in an indirect determination of the alkalies.

III.—LONDON AND MANCHESTER PLATE GLASS.

	I.	II.	MEAN.
Silicic acid	78·0357	77·7827	77·9092
Potash	1·7453	1·7062	1·7257
Soda	12·4373	12·2822	12·3598
Lime	4·7270	4·9816	4·8543
Manganese	traces	traces	traces
Sesquioxide of iron	„	„	„
Alumina	3·5495	3·6502	3·5998
	100·4948	100·4029	100·4488

A table is subjoined containing analyses of several varieties of plate glass, in order that the composition of the plate glass in this country may be compared with that manufactured abroad. The Venetian glass was analysed by M. Berthier, the Bohemian mirror glass by Peligot, and the French glasses by Dumas.*

	Venetian Plate Glass.	Bohemian Plate Glass.	French Plate Glass.		British Plate Glass.	London Thames Plate Glass.	London and Manchester Plate Glass.
			No. 1.	No. 2.			
Silicic acid	68·6	67·7	75·9	73·85	77·36	78.68	77·90
Potash	6·9	21·0	..	5.50	3·01	1·34	1·72
Soda	8·1	..	17·5	12·05	13·06	11·63	12·35
Lime	11·0	9·9	3·8	5·60	5·31	6·09	4·85
Magnesia	2·1	..	..	..	..	..	..
Manganese	0·1	..	..	..	..	..	trace
Oxide of iron	0·2	..	..	..	0·91	trace	..
Alumina	1·2	1·4	2·8	3·50	traces	2·68	3·59
	98·2	100·0	100·0	100·00	99·65	100·42	100·41

Plate glass is usually considered as a double silicate of lime and soda, or of lime and potash. The following atomic expressions represent the different analyses contained in the above table; the amount of potash contained in the English varieties of glass being very trifling, this oxide has been neglected altogether in the construction of their formulæ.

Venetian plate glass	$2\,KO, 3\,NaO, 5\,CaO, 22\,SiO_3$
Bohemian mirror glass	$KO, CaO, 4\,SiO_3$
French plate glass, No. 1	$4\,NaO, CaO, 11\,SiO_3$
French plate glass, No. 2	$KO, 3\,NaO, 2\,CaO, 14\,SiO_3$
British plate glass	$2\,NaO, CaO, 9\,SiO_3$
London Thames plate glass	$2\,NaO, CaO, 8\,SiO_3$
London & Manchester plate glass	$2\,NaO, CaO, 9\,SiO_3$

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* Comp. Knapp's Technology, Vol. II. page 16.

XXIII.—*Researches on the Amyl-Series.*

BY HENRY MEDLOCK, ESQ.

II.

Amylo-urethane.—The original object of my experiments upon the action of chlorocarbonic acid (phosgene gas) on fusel-oil was the formation and study of a compound corresponding to that obtained by Dumas* in the treatment of chlorocarbonic ether with an aqueous solution of ammonia, to which the term urethane, has, by its discoverer, been applied. In a paper, recently communicated to this Society,† I detailed the results of some experiments which seemed to point out the existence of a member in the amyl-series, homologous to chlorocarbonate of ethyl, although the compound in question was of very unstable character; being, in the presence of water, rapidly decomposed into carbonate of amyl with evolution of carbonic and hydrochloric acids. Repeated observations proved that the compound obtained in this reaction could not be heated without suffering partial decomposition. On treating the crude product which had been heated, with ammonia, chloride of ammonium was abundantly formed, together with a small quantity of a fatty substance crystallizing with remarkable facility: the chief portion, however, of chlorocarbonate at my disposal had, evidently, been decomposed under the combined influence of heat and moisture, so that the quantity of the crystalline compound obtained was too small to admit of establishing its composition by analysis, or for the study of its products of decomposition; analogy only allowed me to conclude that it was the urethane of the amyl-series.

It appeared very probable, that by modifying the process in such a manner as to exclude the slightest trace of moisture, the chlorocarbonate of amyl, and by subsequent treatment with ammonia, the urethane likewise might be obtained. In repeating the experiment, perfectly pure fusel-oil was introduced into a glass balloon of 60 litres (about 12 gall.) capacity, filled with dry phosgene gas; rapid absorption took place as was evident by the elevation of temperature, the liquid at the same time assuming a fine amber colour. After being in contact for a quarter of an hour, air was admitted to replace the absorbed gas, a portion of the fluid being immediately transferred to a perfectly dry retort and submitted to distillation. It commenced boiling at 120°

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* Ann. de Chimie et de Phys., T. LIV, p. 225.

† Quarterly Journal Chem. Soc., vol I. p. 368.

(248° F.), the thermometer rapidly rising to 224° (435·2° F.) where it remained tolerably stationary. The fluid distilling over at this temperature, and that also which remained in the retort, no longer solidified on the addition of ammonia, indicating at once that decomposition had taken place. The facility with which my former preparations were decomposed, the peculiar odour of the compound, and the temperature at which it steadily boiled, left no doubt of its being the carbonate of amyl, produced by the action of heat upon the chlorocarbonate; hence it is evident that the latter compound does not admit of being obtained in a state of absolute purity.

The decomposition of the chlorocarbonate into carbonate of amyl, carbonic and hydrochloric acids, in the presence of water, is easily intelligible. In the experiment, however, which I have described, water was excluded with the greatest care. The hydrogen and oxygen, therefore, necessary for the formation of the hydrochloric and carbonic acids, must have been derived from the substance itself. This view is experimentally supported by the large quantity of charred substance which remained in the retort after the distillation.

On treating the remaining portion of chlorocarbonate of amyl, which had not been heated, with an aqueous solution of ammonia, the mixture entered almost into a state of ebullition, evincing a very powerful reaction. The oily liquid floating upon the surface, solidified on cooling, to a crystalline mass, which was subsequently freed from adhering fusel-oil by pressure between folds of bibulous paper, and from chloride of ammonium by washing with distilled water until it no longer affected a salt of silver.

The change which takes place in this reaction is represented in the following equation

$$\underbrace{C_{10}H_{11}O, C_2\left\{\begin{matrix}O_3\\ Cl\end{matrix}\right\}}_{\text{Chlorocarbonate of amyl.}} + 2\ N\ H_3 = \underbrace{C_{10}\ H_{11}\ O, C_2\left\{\begin{matrix}O_3\\ N\ H_2\end{matrix}\right\}}_{\text{Amylo-urethane.}} + N\ H_4\ Cl$$

Amylo-urethane, as I propose to designate this compound, is soluble in alcohol, ether, and boiling water, from which it crystallizes, on cooling, in beautiful iridescent satiny needles. It is fusible at 60° (140° F.), and distils without alteration at 220° (428° F.), the distillate solidifying in the neck of the retort into a fatty crystalline mass.

Analysis gave the following results:

I. 0·4940 grm. of substance burned with protoxide of copper, gave
0·9983 „ carbonic acid, and
0·4418 „ water.
II. 0·3540 „ substance gave

0·6050 grm. of bichloride of platinum and chloride of ammonium, closely coinciding with the formula,

$$C_{10}\,H_{11}\,O,\,C_2\left\{\begin{matrix}O_3\\ N\,H_2\end{matrix}\right\}$$

as will be seen by the following comparison of the theoretical numbers with the experimental results:

	Theory.		Experiment.
12 equivs. of Carbon . .	72	54·96	55·11
13 „ Hydrogen .	13	9·92	9·93
4 „ Oxygen . .	32	24·43	—
1 equiv. of Nitrogen .	14	10·69	10·70
1 „ Amylo-urethane	131	100·00	

By distillation with caustic baryta, amylo-urethane is decomposed into ammonia and carbonic acid, together with an oily product possessing the characteristic odour of fusel-oil, and exhibiting a boiling temperature of about 132° (296·6 F.), which is that of pure hydrated oxide of amyl; in this case, also, the water necessary to accomplish the reaction is furnished by the total destruction of a portion of the substance itself.

Sulphuric acid completely dissolves amylo-urethane in the cold, producing no action upon it whatever, even when allowed to remain in contact for several days, on the addition of water it separates again, forming a crystalline pellicle on the surface of the fluid; if it be heated it is resolved into sulphamylic acid and ammonia, with the evolution of carbonic and sulphurous acids.

The analysis of the baryta-salt gave the following results:

0·2530 grm. dried in vacuo gave
0·1210 „ sulphate of baryta =
0·0712 „ barium.

Agreeing perfectly with the formula:

$$Ba\ SO_4,\ C_{10}\ H_{11}\ SO_4+HO,$$

as may be seen by the following comparison:

	Theory.		Exper.
10 equivs. of Carbon	60·00	24·52	—
12 „ Hydrogen	12·00	4·90	—
9 „ Oxygen	72·00	29·43	—
2 „ Sulphur	32·00	13·09	—
1 equiv. of Barium	68·64	28·06	28·14
1 equiv. of Barium-salt . . .	244·64	100·00	

The opinions held by chemists regarding the constitution of the urethanes are divided; some assume in these compounds the existence of a peculiar acid—carbamic acid; if this view be adopted, the compounds in question will accordingly be considered as the carbamates of methyl, ethyl and amyl; others regard them as carbonic ethers associated with the elements of carbamide. The beautiful investigation of M. Wurtz appeared to offer a new mode of viewing them. The discovery of methylidine and ethylidine and the remarkable analogy of these bases to aniline render it probable that future researches will elicit compounds in the new alkaloidal series analogous to the derivatives of aniline. In fact the compounds corresponding in the methylidine- and ethylidine-series to carbanilide and carbanilamide have actually been obtained. Now the composition of members in these new alkaloidal series analogous to anthranilic or carbanilic acid perfectly coincides with the formulæ of the different urethanes.

Aniline	$C_{12} H_7 N$
Anthranilic acid . .	$C_{14} H_7 NO_4 = C_{12} H_7 N + 2 CO_2$
Ethylidine . . .	$C_4 H_7 N$
Urethane . . .	$C_6 H_7 NO_4 = C_4 H_7 N + 2 CO_2$
Amylidine (?) . . .	$C_{10} H_{13} N$
Amylo-urethane . .	$C_{12} H_{13} NO_4 = C_{10} H_{13} N + 2 CO_2$

It was necessary, and Dr. Hofmann particularly directed my attention to these points, to test this view by the study of the metamorphoses of the new compound; if the formative elements of the urethanes were actually grouped as those in anthranilic acid, amylo-urethane should have yielded, with alkalies, amylidine, and, with sulphuric acid, sulphamylidic acid; repeated trials, however, have proved the results to be as I have above detailed. Hence it appears that this class of compounds are merely isomeric with the true carbamic acids of the new alkaloids which the progress of science will not fail ere long to bring to light.

June 14, 1849.

The President in the Chair.

Wm. Neild, Esq., was elected a Fellow of the Society.

The following alteration in the 14th bye-law was proposed by the Council,—"That no paper shall be read at any meeting of the Society, which has not been in the hands of the Secretary for at least one week previously to the day of meeting; and that no paper once deposited with the Secretary, shall be returned to the author."

The following communications were read:

On the Carbonate of Alumina, by Sheridan Muspratt, Ph.D.—Dr. Muspratt analysed the precipitate produced by carbonate of ammonia in a solution of pure alum; the precipitate was washed until no trace of ammonia remained in the precipitate or filtrate. This precipitate, prior to Mr. Phillips' remarks at the meeting of the British Association at Swansea, had been always described as hydrate of alumina $Al_2 O_3, HO$; the analysis proves that it is a carbonate.

The analytical results are as follows:

0·1600 grms. of substance gave, in Will's apparatus,
0·0095 „ „ carbonic acid.
0·1450 „ „ substance yielded
0·0650 „ „ alumina.

Centessimally represented

	Theory.		Experiment.
3 equivs. of alumina . .	153	44·86	44·82
2 „ „ carbonic acid .	44	12·91	12·19
16 „ „ water . . .	144	42·23	—
	341	100·00	

These results coincide closely with the formula

$$3\,Al_2\,O_3,\ 2\,CO_2 + 16\text{ aq.}$$

On the Manufacture of Soda, and on the Composition of Salt-cake, Black-ash, Soda-ash, and Soda-waste, by Frederick Muspratt *and* Joseph Danson, Esqs.—The authors after describing in this paper the ordinary soda process, introduce the following analyses of the different products of the manufacture.

SALT CAKE AS ANALYSED BY DR. MUSPRATT.

Sulphate of soda	95·936
„ „ lime	0·572
„ „ magnesia . . .	0·136
Chloride of iron	1·357
Sesquioxide of iron	0·291
Insoluble matter	0·400
Water and free acid . . .	1·308
	100·000

COMPOSITION OF BLACK-ASH.

		Calculated on 100 parts without charcoal and sand
Carbonate of soda	26·233	28·890
,, ,, lime	12·913	14·221
Sulphide of calcium	23·479	25·857
,, ,, sodium	0·363	0·399
Chloride of sodium	2·786	3·068
Sulphate of soda	0·743	0·819
Iron, alumina,	5·653	6·226
Phosphate of lime and		
Magnesia*.		
Caustic lime	8·388	9·237
,, soda	7·506	8·267
Silicate of magnesia	1·840	2·026
Charcoal and sand	9·197	—
Water, &c.	0·899	0·990
	100·000	100·000

COMPOSITION OF SODA-ASH.

	Ordinary ash. Brown.	Ash for soap makers. Muspratt.	Ash for plate glass. Danson.
Carbonate of soda	71·614	77·085	78·55
Caustic soda	—	4·881	4·15
Hydrate of soda	11·231	—	—
Sulphate of soda	10·202	5·110	1·70
Sulphite of soda	1·117	—	—
Aluminate of soda	0·923	—	—
Sulphide of sodium	—	0·630	—
Carbonate of lime	—	0·320	—
Sesquioxide of iron	—	0·324	0·27
Carbonate of potash	—	0·200	0·33
,, ,, magnesia	—	—	
Cyanide of sodium	—	—	
Silicate of soda	1·042	2·400	0·25
Chloride of sodium	3·051	7·130	5·62
Sulphide of calcium	—	0·200	—
Charcoal and sand	0·316	0·659	0·48
Water	0·504	1·061	8·65
	100·000	100·000	100·000

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* These constituents of black-ash are not stated in former analyses.—Dr. M.

COMPOSITION OF SODA-WASTE.

			Calculated for 100 parts without charcoal and sand.	
	I. Fresh.	II. Old.[*]	I. Fresh.	II. Old.
Sulphide of calcium	30·835	21·905	25·789	36·698
Bisulphide of calcium	0·520	5·070	5·969	0·618
Carbonate of lime	19·681	35·065	41·202	23·423
Caustic lime	10·110	7·409	8·723	12·032
Iron, alumina Phosphates of lime and Magnesia	6·216	7·572	8·914	7·398
Sulphate of lime	3·857	2·147	2·528	4·590
Silicate of magnesia	1·300	3·080	3·626	1·785
Sulphide of sodium	2·412	1·226	1·443	2·870
Charcoal and sand	15·978	15·060	—	—
Water and loss	9·091	1·466	1·726	10·589
	100·000	100·000	100·000	100·000

In the above analysis, the quantities of carbonate of lime and bisulphide of calcium differ materially. The oxysulphide of lime decomposes readily, giving rise to sulphide and bisulphide of calcium and caustic lime, which latter speedily attracts carbonic acid. *Very old waste*, principally consists of sulphate and carbonate of lime.

June 18, 1849.

Col. Ph. Yorke, in the Chair.

John Shier, M.D., LL.D., was elected a Fellow; and M.M. Boussingault, Chevreul, Gay-Lussac, L. Gmelin, H. Kopp, Laurent, Mitscherlich, Pelouze, Regnault, H. Rose, Thenard, and Wöhler, were elected Foreign Members of the Society.

The following papers were read:

On Chromate of Copper. By H. Sugden Evans, *Student in the Liverpool College of Chemistry*.—When a salt of copper is precipitated by chromate of potash, a yellowish-brown precipitate is produced, which becomes reddish-brown when dried. This salt contains a large and variable quantity of chromate of potash. After being washed for four days, until no soluble matter passed through the filter, the salt was dried and heated to redness, and the author was then enabled to extract considerable quantities of chromate of potash from it, by boiling water. The composition of the brown salt, before being heated and treated with hot water, is stated by the author as follows:

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[*] This waste was about six weeks old; it was dried on a water-bath before being analysed.

Oxide of copper	40·59
Chromic acid	54·62
Potash	1·65
Water and loss	3·14
	100·00

Corresponding to the formula:

$$29\,(CuO, CrO_3), KO, CrO_3 + 10\,Aq.$$

On the quantitative estimation of Cyanogen in analysis. By CHARLES HEISCH, ESQ.—Having occasion to analyse a number of the compounds of cyanogen and mercury, I was led to seek a more ready means of estimating the latter body than that usually adopted, viz., an ultimate analysis.

After one or two trials, I found the following method give such good results that I thought a communication upon the subject might not be unacceptable to the members of the Chemical Society, more especially as it is applicable not only to the analysis of the cyanides of mercury, but to that of many of the double cyanides, such as cobalticyanide of potassium, &c., which have hitherto been analysed by combustion.

The substance to be analysed is put into a small flask, capable of containing from two to three ounces, with some pieces of pure zinc and a little water. A cork is fitted to the flask, perforated with two holes, through one of which a tube-funnel passes to the bottom of the flask, and in the other is fixed a tube, bent twice at right angles; the other end of this tube is dipped into a solution of nitrate of silver. Sufficient sulphuric acid is now added to cause a brisk evolution of hydrogen, when the whole of the cyanogen is converted into hydrocyanic acid, and is carried over into the nitrate of silver, and there precipitated as cyanide of silver. The heat produced by the action is usually enough to drive over all the hydrocyanic acid formed; but should this not be the case, the flask may be heated until no more cyanide of silver precipitates. In dealing with the salts of mercury by this method, it is necessary to add to the sulphuric acid enough nitric acid to prevent the action being stopped by the amalgamation of the zinc.

In proof of the accuracy of this method I may state, that 11·87 grs. of bicyanide of mercury gave 12·554 grs. cyanide of silver: by calculation, it should have given 12·608 grs.

XXIV.—*Examination of some Slags from copper smelting furnaces.*

By Frederick Field, Esq.

The phenomena occasioned by the continued action of heat upon mineral substances in connexion with various fluxes, such as lime, felspar, &c., have been carefully studied by several eminent philosophers, their experiments, I believe, however, have been chiefly confined to the laboratory and to the products obtained within the confines of the crucible in the assaying furnace. Many hundred analyses of slags resulting from all kinds of fluxes employed by the assayer, have been made by M. Bertier, and more recently by Mr. Mitchell, in order to shew the different states of mineral and flux before and after fusion, and their researches have been invaluable to the assayer and practical smelter, throwing considerable light upon the various and oftentimes complicated action resulting at an elevated temperature. The following analyses have been made upon the products of furnaces in which the ingredients were enabled mutually to react upon a more extended scale, the fluxes being at the same time not very unlike those employed by the assayer. The experiments described below will, I hope, not be entirely destitute of interest, phenomena frequently taking place in operations of considerable magnitude, which cannot be observed in the smaller and humbler experiments in the laboratory furnace.

The slags, the analyses of which form the subject of the present paper, were obtained from the furnaces of the South American and Mexican Company in Chile, and the analyses were performed in the laboratory of that establishment. The method of smelting copper carried on at the works of the company, is that patented by Mr. Napier.

When the mineral was mixed with 20 per cent of its weight of common salt, and 15 per cent of lime, and the whole kept in a state of fusion for some time, the slags on being skimmed, presented an uniform mass, perfectly limpid and free from metallic particles, upon cooling, however, the mass separated into two distinct portions, which could be divided from each other with the greatest facility, a slight blow of the hammer being sufficient to cause them to fly asunder: it appeared to me interesting to determine the composition of both portions, in as much as they presented very distinct physical appearances, the lower stratum having a highly crystalline texture very much resembling certain species of syenitic rock, while the upper portion had a fine glassy appearance, totally devoid of crystallization.

This latter which we shall distinguish as No. 1, or glassy slag, possessed a fine dark green colour, closely approaching to black, having exactly the appearance of the glass from which the common wine bottles are manufactured, it presented a highly conchoidal fracture, and was immediately decomposed by aqua regia, and even by boiling hydrochloric acid. A qualitative analysis shewed the presence of silicic acid, alumina, oxide of iron, lime, magnesia, manganese, chlorine, sodium, with traces of sulphur.

The following is its composition in 100 parts.

Silica	49·26
Alumina	12·37
Protoxide of iron	18·60
Lime	7·84
Magnesia	2·62
Oxide of copper	0·70
Chloride of sodium	0·48
Soda	7·93
Manganese	traces
Sulphur	
Loss in analysis	0·20
	100·00

The chloride of sodium was estimated from the amount of chlorine obtained by boiling 200 grains of finely pulverized slag for an hour with distilled water, and subsequent precipitation with nitrate of silver. As the slag was perfectly decomposable by aqua regia, fusion with baryta for the estimation of the soda was unnecessary, that alkali being determined by the method proposed by Heintz, for the separation of magnesia from the alkalies. The lime, alumina, iron, &c., having been separated by carbonate of ammonia, a stream of hydrosulphuric acid was passed through the filtrate previously acidulated, in order to precipitate traces of copper; after boiling with a subsequent addition of ammonia, phosphate of ammonia was added to precipitate the magnesia; an addition of acetate of lead, removed the excess of phosphoric acid, and again the excess of lead was separated by means of a mixture of carbonate of ammonia and ammonia; on evaporation to dryness and subsequent ignition, chloride of sodium remained in the platinum basin, from which the amount existing as such in the slag was deducted, and the soda estimated from the residue. This slag, as before remarked, has a clear glassy structure, and has not the most distant appearance of containing copper. The 0·70 per cent of black oxide found by analysis, is present in combination with silicic acid. In contact with metallic iron, the colour is changed from black to a fine red, owing doubtless to the reduction of the protoxide to the suboxide in the following manner. $2\,(Cu\,O\,Si\,O_3) + Fe = (Cu_2\,O\,Si\,O_3) + FeO\,Si\,O_3$. This phenomenon was always observed when the slag had come in contact with the *rabble* used by the furnace-man, or with the *fore-plate* of the furnace.

The under slag, (No. 2), which is termed sharp or metallic slag, presented a very different appearance from the former, it was undecomposable by aqua regia, and a long continued fusion with carbonate of soda was necessary for its entire decomposition. A qualitative analysis proved the existence of the same substances as in the former specimen. On ignition to whiteness with carbonate of baryta only very small quantities of alkali were observable.

The following is the quantitative analysis of this slag:

Silica	49·60
Alumina	14·00
Oxide of iron	32·94
Lime	1·23
Magnesia	0·11
Oxide of copper	1·06
Soda	0·70
Chloride of sodium	0·43
Manganese	traces.
	100·07

It will be observed that the amount of silica is nearly equal in these two analyses; in the former it is 49·26, in the latter 49·00, but all the other ingredients, the alumina excepted, are in widely different proportions. In fact, slag No. 2 may almost be considered as a silicate of iron and alumina, these three bodies alone forming more than 96 per cent of the whole mass. We may imagine that slag No. 1 acted as a bath from which No. 2 had crystallized; that silica, in certain combinations, with soda, iron, lime, &c., dissolved a silicate containing an excess of iron and deposited it, on cooling, in crystalline forms more or less defined; in other words, that the metallic slag was held in solution in the glassy slag, the latter containing nearly the whole of the soda, lime, and the more fusible compounds. However small the quantity taken from the furnace, the same phenomenon always occurred, viz., the complete separation of a crystalline slag from a homogeneous mass resembling black glass.

When smaller proportions of salt, but the same quantity of lime were employed, viz. 10 per cent of the former, and 15 per cent of the latter, in regard to the mineral of copper, no separation of the slags took place on skimming, but the mass presented a very different aspect to the two former specimens. It was now highly variegated, and had a beautiful serpentine appearance, very much resembling many specimens of igneous rock I have since seen in this country, (Chile), and so hard as to be capable of receiving a beautiful polish. A qualitative analysis gave me the same ingredients as in the two former slags, with the addition of sulphur and unburned carbonaceous matter. This slag, also, had to be decomposed by fusion with carbonate of soda, and the alkali it contained, was estimated by fusing it with baryta. 100 parts gave me:

Silica	42·20
Alumina	10·80
Lime	6·43
Magnesia	2·14
Protoxide of iron	31·00
Oxide of copper	0·45
Chloride of sodium	0·34
Soda	3·44
Sulphur	1·43
Escoria	1·56
Loss in analysis	0·21
	100·00

On examining some escorias from a furnace some few leagues from Coquimbo, I observed, on breaking a portion, beautiful needle-shaped crystals grouped together in large and distinct cubes in one of the cavities, having very much the appearance of those in No. 2, only larger. They were separated, with some difficulty, from the mass, and in qualitative analysis shewed the existence of lime, silica, oxides of iron and copper, alumina and magnesia. Twenty-four grains were analysed and yielded the following per-centage composition:

Silica	35·60
Protoxide of iron	50·46
Alumina	6·85
Lime	4·48
Magnesia	0·16
Oxide of copper	2·32
Loss	0·13
	100·00

The large amount of protoxide of iron is here to be observed, and from many experiments not yet concluded, it appears to me that the other ingredients in the crystals, besides the silica and iron, are not essential to the crystalline structure of the mass, but may be reckoned as foreign substances. I have not, as yet, however, met with any that contained only silicium, oxygen, and iron.

As I am, at present, constantly engaged in investigations regarding the nature of the substances placed in the furnace, and the condition they present after fusion, I trust to be able, at some future time, to lay before the Society a more detailed account of the various silicates obtained. Every different proportion of ingredients, every prolongation of temperature, causes not only a difference in constitution, but an entire change in physical appearance, so that, perhaps, by many careful analyses we may arrive at more satisfactory conclusions regarding the formation of natural silicates and other minerals of igneous origin.

XXV.—*On the Relative Expansions of Mixtures of Alcohol and Water under the influence of a certain rise of Temperature, and on a new instrument for taking the Specific Gravities of the same.*

By G. H. Makins, Esq.

About two years since, I made some experiments upon an instrument described by the Abbé Vidal of Toulon, and called by him the "Ebullioscope Alcoömétrique."

The instrument was designed for estimating the proportion of alcohol in mixtures containing it, and especially in those wherein specific gravity gave false results, in consequence of saccharine or saline bodies being held in solution, which so increased the specific gravity as often to disguise even large proportions of alcohol.

Before going to the immediate subject of this paper, I may just mention the conclusions to which I came with regard to the instrument in question. Having been put before Mr. Bate (the maker of Sikes' hydrometer to the Excise and Customs) as an instrument likely to supersede the hydrometer, from the fact of its embracing indications which the hydrometer itself could not shew, while at the same time the ordinary indications of the latter were readily obtained by it, it became an object to test carefully its effectiveness.

I found, as most persons will anticipate, that the first and greatest objection to the instrument was dependant on the fact of the boiling point of a liquid being so considerably influenced by the state of the barometer at the time of its examination. For, as the latter is high, so will the point of ebullition be high in proportion, and consequently the specific gravity of the alcohol under examination appear lower than it should do.

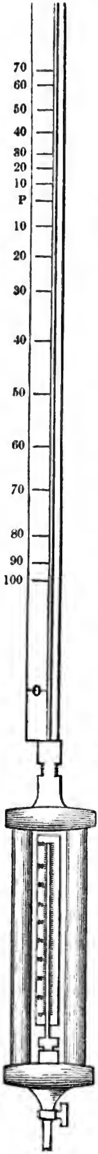
We examined, at the time, the difference in the boiling points, between the barometer points 29·1 and 30·1, in several specimens of alcohol of different degrees of dilution; as examples from these I may mention Excise proof, in which, for the one-inch pressure, there was a difference of 1·4° temperature; and in the case of 70 under proof, (specific gravity 977·2), we found as much as 1·8° for the inch of difference.

A second, and great difficulty, especially to persons not much accustomed to chemical manipulation, as for instance, those using Excise instruments, consists in the extreme care required to read off the degree indicated by the ebullioscope, *just at the moment* of the boiling of the liquid; for, if this be not done precisely at the proper time, evaporation of the spirit speedily takes place, rendering the specific gravity of the mixture very much higher than it was at the commencement of the examination.

The instrument being now constructed under a patent in London, has induced the makers to bestow much care upon its construction, and consequently, to obviate the former evil by an adjustment upon the scale to be regulated by the height of the barometer.

During the time I was engaged on this subject, Mr. Negretti, who had bestowed much care and thought upon the thermometers for the instrument, suggested that another instrument might be made in which the sources of error would be less, and wherein the simple expansion of the spirit by a certain number of degrees of heat would effect the end of ebullition. From some experiments he shewed me, I was induced at once to undertake the examination of the subject with him. I had some hesitation as to whether the incomplete results we have already obtained were worth the attention of the Society, for I am not yet able, from various causes, to communicate the whole of our experiments, but am induced to bring forward that part of them relating to the expansion of spirits, not containing saccharine matter, from the fact of an article having appeared, describing an apparatus for the same purpose, and detailing some results obtained with it, which I do not consider altogether correct; at least, my own conclusions, based on most careful experiments, seem to contradict them. The article I allude to is by Silbermann, and appeared in the "Comptes Rendus" for October 23, 1848; which, by the

FIG. 1.



way, was transcribed into the January number of the "Chemical Gazette."

I will now describe the instrument we employed, as, upon inspection, it may seem a somewhat complicated one to effect an object which might be brought about in a tube similar to the common thermometer tube; indeed, a thermometer bulb and tube on a large scale, furnished with a stopper below for the admission and adjustment of the sample of spirit, would very well answer the purpose. Our instrument consists of a couple of chambers connected by a set of tubes (see Fig. 1); from the upper chamber rises a tube and scale, the former of as uniform bore as could be procured, and to the lower is attached a small stopcock. The form given to the instrument was adopted in order to afford as large a metallic surface as possible, so as to heat a badly-conducting fluid quickly and uniformly, and its parts were so shaped and put together that the free exit of any portions of air which might enter with the spirit by the stopcock was ensured. A thermometer was placed in the interior for shewing the temperature more correctly of the enclosed spirit.

This last is a point of some importance to the results afforded, and I may instance what I have frequently observed in taking the specific gravity of alcoholic liquids and similar badly conducting fluids, viz. that a thermometer will often indicate a difference of a degree *or more* in different parts of a thousand grain bottle, according to the manner in which the bottle has been filled. In using the instrument, our plan was to fill it slowly by gradual depression in a tall vessel containing the specimen for examination. A slight shaking then sufficed to dislodge any air which might have been adherent to the sides of the tubes, &c., after which the zero point was carefully adjusted by means of the stopcock. This having been effected, the temperature of the whole was brought to 62^0 F. by means of immersion in a large vessel of water at that temperature. It was then quickly plunged into a second vessel containing water at 92^0 F., and agitated until the thermometer in the instrument indicated this rise of 30^0 F., when the expansion was carefully noted.

The actual expansions are here, of course, not observed, no allowance being made for that of the instrument itself, which is considerable, and diminishes, by just its amount, that of its contents; all that is here ascertained being the relative dilatation of the several specimens of different specific gravity.

Attention may here be drawn to the difference in the amount of expansion for the same number of degrees increase of temperature, when this increase is in different parts of the thermometric scale. And again, that this difference increases as the proportion of alcohol in a mixture is diminished. In the case of proof spirit, for example, I found that between 60° and 90° F. an expansion indicated by a rise of 6·48 inches on the scale was obtained, while between 90° and 120° F. it increased to 6·84 inches.

The most convenient temperature for operating was between 62° and 92° F., and a number of specimens were first very carefully prepared, to agree with the indications of Sikes' hydrometer, or as nearly as possible to these. The spirits were allowed to stand 48 hours after mixing before being subjected to expansion, and the laboratory was kept as nearly as possible at 62° F.

We commenced with the examination of distilled water, (the 100 point of Sikes), the water having been previously boiled, so as to expel any air contained in it. The stem and body of the instrument happened to be so proportioned as to give a rise of 1·47 inches for the 30° of difference of temperature; and the time occupied in thoroughly heating the water amounted (generally) to about one minute. As distilled water formed our starting point of comparison, we repeated the experiment with it several times with every possible care, but uniformly with the same results.

The measurements of the expansions of the samples we examined, each ascending by 10° of Sikes' hydrometer, are given in the table below:

		Inches.
90	under P. gave an increase of	1·72
80	. . . . . .	2·10
69·9	. . . . . .	2·69
60	. . . . . .	3·30
50·1	. . . . . .	3·96
39·7	. . . . . .	4·69
30·1	. . . . . .	5·32
20	. . . . . .	5·78
10·7	. . . . . .	6·18
Proof	. . . . . .	6·48

The experiments upon this last and upon water, as also upon the specimen 70° over proof, which I shall have to mention, were several times repeated, but the same amount of expansion was uniformly obtained.

Then to pass to over-proof specimens.

FIG. 2.

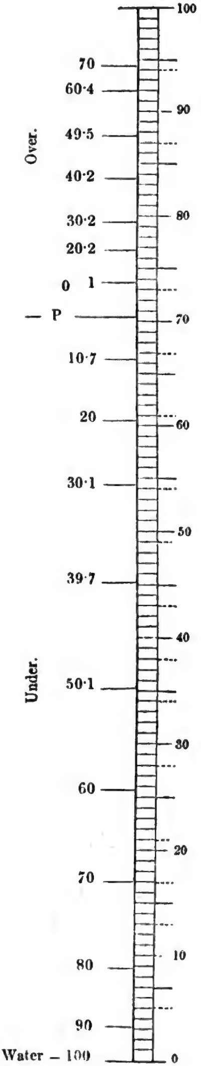
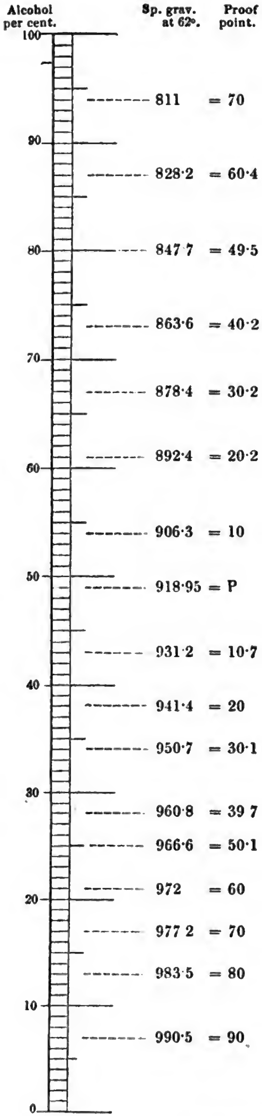

100
70
60·4
90
Over.
49·5
40·2
30·2
80
20·2
0 1
— P
70
10·7
20
60
30·1
50
39·7
40
Under.
50·1
30
60
20
70
80
10
90
Water – 100
0

FIG. 3.


Alcohol per cent.
Sp. grav. at 62°.
Proof point.
100
811 = 70
90
828·2 = 60·4
80
847·7 = 49·5
863·6 = 40·2
70
878·4 = 30·2
892·4 = 20·2
60
906·3 = 10
50
918·95 = P
931·2 = 10·7
40
941·4 = 20
950·7 = 30·1
30
960·8 = 39·7
966·6 = 50·1
972 = 60
20
977·2 = 70
983·5 = 80
10
990·5 = 90
0

		Inches.
10	over P. rose to	6·72
20·2		6·94
30·2		7·15
40·2		7·43
49·5		7·72
60·4		8·03
70		8·13

We stopped our examination at 70° over proof. I have here constructed a scale, which, for distinctness, is divided into two parts. In the first (Fig. 2), the assumed expansion of anhydrous alcohol for the 30° of increase of temperature between 62° and 92° is shewn. This space is divided into 100 equal parts, each part representing 1 per cent. of alcohol; at the side are placed the expansions of specimens (each descending by 10° of Sikes') from anhydrous alcohol to water. The zero point (Fig. 1) has been omitted in the scales, to diminish their length; it should be placed 1·47 inch below the first division, and represents the height to which the stem of the instrument was filled in each case, previous to expansion. Alcohol, of 70° over proof, consists of about 6 parts water to 94 of alcohol, so that in the construction of the table, this expansion of alcohol of 70° over P. has been divided into 94 equal parts, each division representing 1 volume of alcohol; to these 94, 6 divisions have been added to make up 100, thus completing the range between water and anhydrous alcohol.

The second scale (Fig. 3) is similarly divided into 100 parts, and opposite these divisions, at their proper points as to proportions of alcohol and water, are ranged the several proof points examined, with their specific gravity at 62° F.

On comparing the two tables, a gradual increase will be observed in the rate of expansion from some points, and a decrease from others; and these amounts of increase and decrease do not in any way correspond to the relative quantities of alcohol and of water in the mixtures, but are totally independent of them.

Now from Silbermann's paper, you might be led to a very different conclusion, viz. to this: that the expansion takes place at a uniform rate of increase, corresponding to the increasing proportions of alcohol, for he says, "If a series of mixtures of alcohol and water be made, beginning with water, 100 parts, alcohol 0; water 99, alcohol 1; water 98, alcohol 2; water 97, alcohol 3, &c.; up to water 0, alcohol 100; and their several points of elevation at the respective temperatures of 25° and 50° (cent) be carefully marked on the tube, a complete centessimal alcoholometric scale will be produced, which will indicate the quantity of alcohol contained in any mixture of alcohol and water by introducing it at 25^0, and afterwards heating it up to 50^0."

If the measurements I have given are compared, it will be found that they are in an increasing ratio up to 40 under proof (which contains about 28 alcohol + 72 water); they then decrease somewhat rapidly to 30 over proof. A third change then takes place, and they again increase to 60 over proof. And lastly, they again decrease very rapidly to 70 over P.; and possibly to anhydrous alcohol, though from the various sources of error in observations on very strong alcohol, we did not use it above 70 over proof: that is to say, of a specific gravity of 0·811 at 62^0.

Now, if all this be true, and I may state that every possible precaution was observed to ensure the accuracy of the experiments, it becomes a question to determine why these expansions do not take place just in the proportion of the alcohol contained in the respective mixtures, or, in other words, why certain regular variations in the rate of expansion take place about certain points in the scale. I believe the answer may be satisfactorily given in a few words; namely, that the expansions depend on the existence of certain definite hydrates of alcohol, which hydrates are formed somewhere near the proportions at which these changes occur.

In conclusion I must repeat, that the experiments I have described were undertaken some two years since, and having been prevented carrying them fully out at the time, I did not intend to bring them before the Society until they had been brought into a much more definite form, by repeating them on mixtures containing alcohol in regularly increasing proportions; but the appearance of the paper I have mentioned compels me to put them, incomplete as they are, into the form of a notice, hoping, as I do, to work the subject fully out, and having done so, to bring it again before the Members.

I may mention that the instrument we have used, (or a more simple modification of it), affords a very ready and accurate means for the determination of the specific gravity of such mixtures, and is, I believe, much more likely to be useful than the common glass hydrometer now so much employed for the purpose.

The sensibility may, of course, be augmented by increasing the proportion of the chamber as compared with the tube, always taking care not to have the latter so small as to be influenced to any great extend by capillary action: again, by using a greater range or higher temperature: and, lastly, by making the chamber of such form and material as shall yield but little to expansion, and consequently exert a lesser influence upon the expansion of the liquid contained in it.

Mr. Negretti is now making the instrument in a simple and inexpensive shape for such purposes.

XXVI.—*On some new Acids contained in the Oil of the "Bassia Latifolia."* By T. F. Hardwick, Esq., *Student in King's College, London.*

COMMUNICATED BY DR. MILLER.

The rapid advances that have been made of late, in that department of Organic Chemistry which embraces more particularly the constitution of the vegetable oils and fats, are too well known to need remark; it has been shown that not only does each of these bodies, with few exceptions, contain a distinct and peculiar acid, but that these different fatty acids are nearly allied in chemical constitution; speaking generally, they may be represented by the formula $CH_n + O_4$.

The object in undertaking the present investigation, was to determine the composition of one of these vegetable oils, the produce of "Bassia Latifolia;" from the results obtained, it appears that an acid exists in this substance which has not hitherto been found elsewhere; this acid to which it is proposed to apply the name of "Bassic acid" may be isolated with comparative facility.

I am much indebted to Professor Royle, for procuring me a specimen of the Oil of Bassia in considerable quantity. The following particulars with regard to the tree from which it is obtained are gathered from his excellent " Illustrations of Himalayan Botany."

The Bassia Latifolia belongs to an important genus of plants, which are found along the central range of the Himalayan mountains, and in the northern and southern provinces of India.

The most common species of this genus are the Bassia Latifolia and Longifolia, or Illupei tree, both of which are extremely valuable in an economical point of view; not only is their wood in much request as timber, but they yield parts useful in medicine, and their fleshy berry-like flowers are eaten by the natives. Those of the Bassia Latifolia, moreover, are subjected to fermentation, and a powerful and cheap spirit is distilled from them. The Oil is procured from the seeds by expression, and is much used as a substitute for cocoa-nut oil, in cooking, and for making soap.

The Bassia Butyracea of the Almora Hills is a species less commonly met with; it is characterized by furnishing a concrete oil, of a white colour, and very delicate flavour; it is probably analogous to the shea, or butter tree, of Mungo Park, which is described by him as closely resembling the Bassia Latifolia.

PROPERTIES OF THE "OIL OF BASSIA."

Bassia oil is of a yellow colour, but is gradually bleached on exposure to light; it possesses a faint, though not disagreeable odour, and has somewhat the consistence and appearance generally of ordinary butter; its specific gravity is 0·958°; on the application of heat, it begins to soften about 75° Fahr., and at 80° to 85° is almost entirely liquid. Alcohol, sp. gr. 0·840, hardly affects this oil; anhydrous alcohol dissolves it sparingly, but deposits the whole, or the greater part, on cooling; it is abundantly soluble in ether, both hot and cold, and is saponified by potash or soda without difficulty. With regard to its chemical constitution, it may be briefly stated, that it contains a liquid acid, the oleic, in considerable quantity, and also two solid fatty acids of different melting points, which form the subject of the present paper. On distillation, it yields an abundance of acroleine, and, by the action of oxide of lead, a substance may be procured from it, which has all the properties of glycerin.

PREPARATION OF "BASSIC ACID."

In the preparation of this acid, the oil was saponified by a weak solution of caustic soda, and the soap separated by common salt once or more in order to whiten it, it was then re-dissolved in water and decomposed by hydrochloric or tartaric acid. I found the latter of these the most efficacious, it separates the acid in a much shorter time, and does not render it yellow, which hydrochloric acid is apt to do. The mixed fatty acids, as thus obtained, were found to have a fusing point of about 112° Fahr. (44·5°C); the fatty mass was next submitted to pressure, in order to separate as much of the oleic acid as could in that way be squeezed out, and the solid portion afterwards crystallized six or eight times from alcohol, to attain the same object more completely. When the melting point has risen as high as 135° (57·2° C), it becomes quite constant, and as I found moreover that it was not in any way altered by the use of coal-naphtha, pyroligneous spirit, or rectified oil of terpentine, I was at first induced to suppose it to be a pure substance; this however is not the case.

If the mixed acids, as obtained by crystallization from alcohol of a melting point 135°, be repeatedly crystallized from ether, the melting point rises, rapidly at first, afterwards more slowly, until at length it becomes fixed at 159° (70·5° C), and is not affected by any further treatment. I found that in this process two pounds of the oil yielded about eight ounces of mixed acids, free from oleic acid, and rather more than half an ounce of the Bassic acid in a state of purity.

Bassic acid, as thus obtained, is a very white crystalline substance perfectly tasteless and inodorous, it does not feel greasy and is easily pulverized; its solution in alcohol reddens litmus.

By analysis with chromate of lead, it yielded the following numbers.

I. 6·37 grains gave 17·76 CO_2 and 7·34 HO
II. 3·61 „ 10·09 CO_2 „ 4·2 HO.

which give in 100 parts:

	I.	II.
Carbon	76·04	76·22
Hydrogen . . .	12·8	12·92
Oxygen . . .	11·16	10·86
	100·00	100·00

These analyses agree with the formula $C_{36} H_{36} O_4$.

	Atomic weight.	Theoretical per-centage.
C_{36} . . .	216	76·06
H_{36} . . .	36	12·78
O_4 . . .	32	11·26
	284	100·00

DISTILLATION OF BASSIC ACID.

Bassic acid is volatile without change, if the heat be carefully regulated. I found the best way to effect the distillation was to immerse the retort in a bath of fusible metal, or what answers as well, of tin and lead in the proportions to form plumber's solder; the acid then distils over perfectly white, and so little decomposition takes place that the melting point is lowered no more than one or two degrees. If instead of the metal bath, the heat of a common lamp be used, although the distillation appears to proceed as before, without interruption, yet on examination, the product will be found to consist almost entirely of liquid carbo-hydrogens, with hardly a trace of acid; to complete the purification, the distillate is to be crystallized a few times from alcohol, until the melting point rises to 159°, and afterwards its solution in ether allowed to evaporate spontaneously; by this means, the acid is deposited in beautiful rhombic plates, which are perfectly clear and transparent, and on one occasion were as much as ¼ inch in the side. The melting point of these crystals is exactly the same as that of the acid itself, with which the numbers they yield on analysis show them to be identical.

3·54 grains gave 9·8 CO_2 and 4·04 HO,

which correspond to

	Centismally.	Theoretical.
Carbon	75·71	76·06
Hydrogen	12·71	12·78
Oxygen	11·58	11·26
	100·00	100·00

BASSIATE OF POTASH.

This salt may be formed by boiling the acid with a solution of carbonate of potash, and evaporating to dryness: on digesting the residue in strong alcohol, the Bassiate of potash dissolves, leaving behind the excess of carbonate, and may be procured pure by distilling off the spirit;—it is a white powder, having a soapy feel, and does not deliquesce on exposure to air; with water it forms a gelatinous mass, but dissolves perfectly both in alcohol and ether; it crystallizes out on cooling, in innumerable small needles which cross each other in every direction, and when pressed and dried, have a glistening aspect; this crystallization is by far the most perfect from an ethereal solution, and in using the Bassiate of potash as a means of preparing the corresponding silver and baryta salts, by which the formula and atomic weight of the acid are to be determined, it is well to take advantage of it, and ensure the purity of the salt; in this way traces of fatty matter are removed which still adhere to the acid, and which, although not sufficient in quantity to affect its melting point, or the numbers it yields on analysis, may yet interfere with the determination of metallic silver, or of baryta; that this impurity does exist is shown by the acid itself, as well as by the potash salt prepared from it, giving a somewhat milky solution with alcohol, whilst the distilled acid or the crystallized salt, are both perfectly and entirely soluble. Perfectly pure ether should not be used, as the salt is almost insoluble in this, but ether containing alcohol in such proportion as to have a specific gravity of about 0·745; the rectified ether of the pharmacopœia answers very well.

BASSIATE OF SODA.

This is prepared in a similar way to the last mentioned salt; it is white and hard, having altogether the appearance of a soap; it is scarcely at all affected by cold water, and difficultly soluble in warm; alcohol takes it up freely; it does not however crystallize on cooling, but forms a gelatinous mass.

BASSIATE OF SILVER.

Bassiate of silver may be prepared by decomposing an alcoholic solution of pure, crystallized, Bassiate of potash by nitrate of silver; it falls as a curdy mass, which requires very careful washing with distilled water, in order to free it entirely from all traces of the precipitant. When dry, it is a very loose and bulky powder, exhibiting no appearance of crystalline structure, and slowly darkening in colour on exposure to light.

By analysis, the following results were obtained:

I. 6·14 grains gave 12·32 CO_2 and 5·06 HO
II. 7·03 ,, 14·11 CO_2 ,, 5·7 HO
III. 6·61 ,, 13·33 CO_2 ,, 5·41 HO

which give in 100 parts:

	I.	II.	III.
Carbon . . .	54·72	54·74	55·00
Hydrogen . . .	9·16	9·01	9·09
Oxygen and Silver .	36·12	36·25	35·91
	100·00	100·00	100·00

I. 9·47 grains when ignited left 2·61 silver
II. 12·47 ,, 3·45 ,,

these correspond in 100 parts to:

	I.	II.
Silver	27·56	27·67

and lead to the formula AgO, C_{36} H_{35} O_3

	Atomic weight.	Calculated.
C_{36}	216	55·24
H_{35}	35	8·95
O_4	32	8·19
Ag	108	27·62
	391	100·00

BASSIATE OF BARYTA.

This salt is precipitated on dropping a solution of chloride of barium into an alcoholic solution of Bassiate of potash; it is very white, not so bulky as the silver salt, and has a glistening semi-crystalline appearance; it is insoluble both in alcohol and ether.

It gave on analysis the following quantities:

I. 6·17 grains gave 13·80 CO_2 and 5·43 HO
II. 5·1 „ 11·42 CO_2 and 4.66 HO

which yield on 100 parts.

	I.	II.
Carbon . . .	61·00	61·07
Hydrogen . . .	9·78	10·02
Oxygen and baryta .	29·22	28·91
	100·00	100·00

I. 10·55 grains left on ignition 3·00 BaO CO_2
II. 16·24 „ 4·65 BaO CO_2

giving as the per-centage of baryta—

I.	II
22·07 . .	22·21.

The formula for the baryta salt of bassic acid requires, BaO, $C_{36}\ H_{35}\ O_3$.

	Atomic weight.	Calculated.
C_{36} . .	216 . .	61·36
H_{35} . .	35 . .	9·94
O_3 . .	24 . .	6·83
BaO . .	77 . .	21·87
	352	100·00

BASSIATE OF LEAD.

Like the lead salts of the fatty acids generally, this salt is a light, white powder, insoluble in water, alcohol, and ether; it is procured by decomposing Bassiate of potash with acetate of lead.

CHLORO-BASSIC ACID.

If a constant stream of dried chlorine gas be passed through a portion of Bassic acid, kept by a water-bath at a temperature of 212°, an interesting series of changes takes place; the acid first becomes very liquid, and almost as limpid as water, then, after remaining in this state for a short time, slowly and by degrees it thickens, until it gets viscid like gum, and at length is entirely converted into a slightly yellow resinous looking body, which on cooling solidifies, and is easily pulverizable; it is quite transparent, and has a well marked vitreous fracture. The action of the gas is slow, and must be continued for two or three weeks, until the vapour of hydrochloric acid gas is no longer perceptible, and a piece of moistened litmus paper is bleached by the excess of chlorine.

By analysis it yielded the following numbers:

I. 7·2 grains gave 9·12 CO_2 and 2·84 HO
II. 6·90 „ 8·75 CO_2 „ 2·74 HO

on 100 parts:

	I.	II.
Carbon	34·56	34·19
Hydrogen	4·38	4·36
Chlorine and oxygen	61·06	61·45
	100·00	100·00

By igniting the acid with lime, dissolving the product in nitric acid, and precipitating with nitrate of silver,

7·7 grains gave 17·84 Ag Cl.

equivalent to

Chlorine 57·16 per cent.

These analyses agree with the formula:

	Atomic weight.	Theoretical per-centage.
C_{36}	216	34·06
$\left\{\begin{matrix} H_{26} \\ Cl_{10} \end{matrix}\right.$	26 360	4·10 56·78
O_4	32	5·06
	634	100·00

It appears, therefore, that a substitution of a certain number of equivalents of chlorine for an equal number of hydrogen has taken place, the general frame-work of the formula remaining unaltered, and this view is further supported by an examination into the properties of the newly-formed substance. Not only is it acid to test paper, but it forms insoluble salts with lead, baryta, &c., either of which may be formed by dissolving the acid in alcohol, and dropping in a solution of acetate of lead, or of chloride of barium; so again, if a small portion of the powdered acid be digested in a cold solution of carbonate of potash, it is quickly saponified, forming a white flocculent soap, almost insoluble in cold water, but easily dissolved by alcohol; I quite failed however in every attempt at crystallizing this Chloro-bassiate of potash, it seems perfectly amorphous, as indeed is the acid itself.

The following is a list of the compounds of bassic acid, that I have hitherto examined.

Bassic acid		$C_{36}\,H_{36}\,O_4$
Bassiate of potash		
,,	soda	
,,	silver	$C_{36}\,H_{35}\,O_4\,Ag$
,,	baryta	$C_{36}\,C_{35}\,O_4\,Ba$
,,	lead	
Chloro-bassic acid		$C_{36}\left\{\begin{matrix}H_{26}\\Cl_{10}\end{matrix}\right.O_4$

The analyses of these are quite conclusive as to the formula of the acid, and prove it beyond a doubt to be a member of that series before alluded to, as characterized by containing $(CH)_n + O_4$, it stands immediately above Margaric acid, which until recently, was the highest known.

Myristic acid	$C_{28}\,H_{28}\,O_4$
* * *	
Palmitic acid	$C_{32}\,H_{32}\,O_4$
Margaric ,, ...	$C_{34}\,H_{34}\,O_4$
Bassic ,, ...	$C_{36}\,H_{36}\,O_4$
* * *	
* * *	
Cerotic acid, &c. . . .	$C_{64}\,H_{54}\,O_4$

Volatility without change is an important character of this series, and one not found in any fatty acid that does not belong to it; it has been shown that Bassic acid is not only volatile, but may by careful distillation be procured in a purer and more perfectly crystalline form than by any other method. It would be interesting to find whether or not the glycerin compound of this acid could by any means be separated from the original fat. I have not as yet succeeded in effecting this, but its actual presence may be easily demonstrated by boiling out a portion of the oil with alcohol for a considerable time, in order to remove the liquid oleine as far as may be: on cooling, crystals will be found scattered about here and there in globular masses; they are harder and more white than the surrounding fat, and have a higher melting point.

BASSIA ACID OF LOWER MELTING POINT.

I now proceed to give in detail the course pursued with regard to that portion of the mixed acids, melting at 135°, from which the Bassic acid had been in a measure separated.

The treatment with ether was continued as before, but with this important variation from the original arrangement, that the different crops of crystals as they were successively formed, were rejected, and the solution retained; the object being to remove, by degrees, the whole of the Bassic acid in virtue of its inferior degree of solubility. When the melting point of the acid which crystallizes out becomes fixed, it is evident that nothing further will be gained by continuing the process, and therefore what remains of the ethereal solution may be evaporated in order to procure the acid it contains in a solid form. The melting point of this compound ranges between 129° and 131° (54°—55° C.), but is easily affected by the action of caustic alkalies and also of alcohol; this indicates the presence of small quantities of fatty matter and oleic acid, both of which being extremely soluble in ether, would of necessity be left in the last mother liquor. I found that the only way to remove these impurities effectually, was to submit the whole to distillation, which as before, must be conducted in a metal bath in order to equalize the distribution of heat; the distillate when freed from liquid carbo-hydrogens by alcohol, has a fusing point of 132° to 134°, and is the desired acid in as pure a state as I have been able to procure it.

With regard to the properties of this substance, it is not so perceptibly crystalline in its structure as Bassic acid, but more homogeneous and wax-like; if a drop of its solution in alcohol be allowed to evaporate, or a small portion of the acid itself be melted over the surface of a glass plate, so as to form a thin film, it presents on solidifying, the curious appearance of a series of concentric rings, which may not unaptly be compared with a section of bone under the microscope. These characteristic rings are observed both before and after distillation, and also in the mixed acids of 135° melting point, but disappear in the Bassic acid, as it approaches to a state of purity; an ethereal solution of this acid, on spontaneous evaporation, deposits it in warty and granular masses, which melt as before, between 132° and 134°. With the various metallic oxides it forms salts, all of which may be formed in a similar manner to the corresponding compounds of Bassic acid; the salt of potash is soluble both in alcohol and ether, and crystallizes from the latter solvent, in tufts of needles much resembling the crystallized Bassiate of potash; these needle-like crystals when decomposed by tartaric acid, yield a product melting as before at 132° to 134°; the baryta and lead salts are both quite insoluble.

By analysis the following numbers were obtained :

I. 4·4 grains gave 12·01 CO_2 and 5·01 HO
II. 4·69 grains gave 12·83 CO_2 and 5·44 HO

or in 100 parts:

	I.	II.
Carbon	74·44	74·61
Hydrogen	12·65	12·65
Oxygen	12·91	12·74
	100·00	100·00

The silver salt prepared by the action of nitrate of silver on the crystallized potash salt yielded as follows:

I. 5·99 grains gave 11·81 CO_2 and 4·72 HO
II. 5·96 grains gave 11·7 CO_2 and 4·69 HO

in 100 parts:

	I.	II.
Carbon	53·77	53·54
Hydrogen	8·75	8·74
Oxygen and silver	37·48	37·72
	100·00	100·00

By ignition,

I. 10·11 grains gave 2·94 metallic silver
II. 14·44 grains gave 4·23 metallic silver

centesimally represented:

	I.	II.
Silver	29·08	29·29

These analyses correspond somewhat with the formula for Palmitic acid $C_{32}\ H_{32}\ O_4$, which requires, in 100 parts :

Carbon	75·00
Hydrogen	12·50
Oxygen	12·50
	100.00

The silver salt of the same acid requires :

Carbon . .	52·89
Hydrogen . .	8·54
Oxygen . .	8·87
Silver . . .	29·70
	100·00

Both the melting point of the acid itself, however, and its properties in general, quite disprove the idea of its identity with Palmitic acid. The most probable view of the case seems to me that the true formula of the acid is $C_{30}\,H_{30}\,O_4$, intermediate in the series between Myristic and Palmitic acids, and that a portion of Bassic acid is still present as an impurity, the variation occasionally observed in the melting point strengthens this assumption, but, after a careful study of the various salts formed by this acid, I have been as yet unable to effect any further purification or separation of Bassic acid than that above detailed.

XXVII.—*Researches on Strychnine.*

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I.—ON THE COMPOSITION OF STRYCHNINE AND OF ITS SALTS.

In his researches on the aniline series, Dr. Hofmann communicated some experiments upon the action of iodine on aniline,* which terminated in the formation of iodaniline, a substitution-product, possessing, like chloraniline and bromaniline, the basic character of the original atom. Incidentally to this investigation, Dr. Hofmann recalls the experiments upon the action of iodine on various natural alkaloids, which had been formerly undertaken, and had led to very different results. It was upon this ground that he invited us to subject the results of former enquiries to a new examination.

Various chemists have examined the behaviour of iodine with organic alkaloids. Pelletier† obtained by the action of this element on strychnine, brucine, cinchonine, quinine, morphine, and codeine, a series of substances, the study of which led him to the conclusion that they were compounds of the original bases, with one or two equivalents of iodine, corresponding to the compounds of ammonia with that element. His results, with reference to brucine and strychnine at least, have been subsequently confirmed by Regnault.[*]

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* Mem. Chem. Soc. London, Vol. III. p. 269.

† Liebig's Annalen, Vol. XXII. p. 113.

A similar class of compounds has been produced by Bouchardat,[†] who studied the action of iodine upon the salts of strychnine. He considered these substances to be the hydriodates combined with more or less iodine, analogous to the iodinated iodides of potassium and ammonium.

Among the various compounds elicited in these several investigations, those of strychnine appeared to be the most definite. This circumstance, as well as the facility with which both strychnine and its salts may be obtained in a state of perfect purity, induced us to select this body for our experiments.

We succeeded without difficulty in preparing the iodinated compounds described by Pelletier; on submitting, however, several of these substances to analysis, the quantities of carbon and hydrogen found, were invariably below the theoretical numbers of the formulæ, calculated from the generally adopted composition of strychnine. Convinced by the constancy of our results, obtained with a variety of preparations, of the definite nature of the compounds, we were compelled to seek for the cause of the deficiency in the composition of strychnine itself.

This substance has been analysed successfully by Liebig, Regnault and Gerhardt, whose numbers calculated according to the new equivalents carbon and hydrogen, are appended in the following table, together with the formulæ deduced by these chemists from their results.

	Liebig.			Regnault.				Gerhardt.	
	$C_{30} H_{16} N O_3$[‡] | $C_{44} H_{23} N_{1\frac{1}{2}} O_5$[§]			$C_{43} H_{23} N_2 O_4$[‖]				$C_{44} H_{24} N_2 O_4$[¶]	
	Theory.	Experiment.	Theory.	Theory	Experiment.			Theory	Expt.
					I.	II.	III.		
Carbon . .	76·92	75·62	75·86	75·66	74·69	74·96	74·63	75·86	75·54
Hydrogen .	6·83	6·68	6·60	6·74	6·86	6·69	6·89	6.89	6·99
Nitrogen .	6·00	5·70	6·04	8·21	8·43	8·46	—	8·06	8·10
Oxygen . .	10·25	—	11·50	9·39	—	—	—	9·19	—
	100·00	—	100·00	100·00	—	—	—	100·00	—

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[*] Liebig's Annalen, Vol. xxix 58.

[†] Comptes rendus, T. ix. 475.

[‡] Liebig's Annalen, V. xxvi. p. 17. [§] Idem. V. xxvi. p. 58. [‖] Idem. V. xxvi. p. 18.

[¶] Traité de Chimie organique, par M. Liebig, traduit par M. Gerhardt, vol. ii. p. 664. Recherches sur la Classification Chimique des substances organiques, par M. Gerhardt, page 49.

Besides the above, other formulæ have been quoted at different periods. Liebig,[*] from a determination of platinum in the double salt of bichloride of platinum and strychnine, has corrected Regnault's formula to

$$C_{44} H_{23} N_2 O_4.$$

Subsequently Regnault in a letter to Liebig[†] has proposed the formula,

$$C_{42} H_{22} N_2 O_4$$

finding it agree better with the equivalent obtained from Liebig's platinum-determination, and with his own analysis of the hydriodate, than the above corrected formula. Gerhardt, in his translation of Liebig's Organic Chemistry, has likewise made several statements respecting the composition of this alkaloid. After having declared himself in favour of the formula referred to in Regnault's letter to Liebig[‡], he finally adopts the expression quoted in the above table[§].

The difficulty of arriving at any conclusion as to the correct formula of strychnine from such contradictory statements, induced us to repeat the analysis of this body. A simple determination of the elements appeared to be of little assistance in the construction of the formula, if we consider that the different expressions above quoted, with the exception of Liebig's first, are principally based upon analyses, exhibiting no greater discrepancies than about four tenths of a per-cent in the carbon and hydrogen. Hence it became necessary to control the results by an extensive examination of the salts of this base, and also by a careful study of its products of decomposition. In this paper it is our intention to detail the analysis of strychnine and a number of its compounds, reserving for a future communication a description of the products of substitution and decomposition.

The strychnine employed in our experiments, obtained from the laboratory of Mr. E. Merck, of Darmstadt, was crystallized in beautiful four-sided prisms, requiring but one recrystallization from dilute spirits to render it absolutely pure.

Analysis of strychnine.—The combustion of strychnine in the ordinary manner did not present any difficulties; in fact, we found, contrary to the statements of many chemists, that this base and its salts burn with the greatest facility.

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[*] Liebig's Annalen, Vol. xxvi. 57.

[†] Idem. Vol. xxix. 58.

[‡] Gerhardt's translation of Liebig's Traité de Chimie organique, Vol. ii. p. 558.

[§] Idem. Vol. ii. p. 664.

I. 0·2947 grm. of substance burnt with oxide of copper gave:
0·8143 „ „ carbonic acid, and
0·1817 „ „ water.
II. 0·3179 „ „ substance gave:
0·8783 „ „ carbonic acid, and
0·1935 „ „ water.
III. 0·4145 „ „ substance gave:
0·2462 „ „ water.
IV. 0·4038 „ „ substance burnt with chromate of lead and chlorate of potash yielded:
1·1172 „ „ carbonic acid, and
0·2420 „ „ water.
V. 0·6015 „ „ substance burnt with soda-lime, gave:
0·3615 „ „ platinum.
VI. 0·6043 „ „ substance gave:
46· C.C. of moist nitrogen, Bar. 759$^{\text{mm}}$·4′, Therm. 18° C.

Per-centage composition:

	I.	II.	III.	IV.	V.	VI.
Carbon . . .	75·35	75·34	—	75·45	—	—
Hydrogen . .	6·85	6·76	6·59	6·65	—	—
Nitrogen . .	—	—	—	—	8·52	8·81

These numbers agree better with the formula:

$$C_{42}\,H_{22}\,N_2\,O_4$$

than any other proposed, as the following comparison with the theoretical numbers will show:

	Theory.		Mean of expt.
42 equivs. of Carbon . . .	252	75·44	75·38
22 „ „ Hydrogen . .	22	6·58	6·71
2 „ „ Nitrogen . . .	28	8·38	8·66
4 „ „ Oxygen . . .	32	9·60	—
1 „ „ Strychnine . .	334	100·00	

In order to prove the accuracy of the above determinations, and for the control of the formula derived therefrom, we submitted the double compound of strychnine with bichloride of platinum, terchloride of gold and protochloride of palladium to a careful analysis with reference to their metallic elements. The mean of these analyses, which we shall hereafter give in detail, lead to an expression closely corresponding with the equivalent of strychnine when represented by the above formula:

Equivalent deduced from the mean of ten determinations of platinum	337·1
Equivalent deduced from the mean of three determinations of gold	331·6
Equivalent deduced from the mean of two determinations of palladium	338·0
Mean	335·5
Theoretical equivalent . . .	334·0

SALTS OF STRYCHNINE.

The characters of many of the compounds of strychnine are enumerated in most chemical manuals. Of these we shall merely give the analytical results, confining ourselves to a description of such salts only as have not previously been fully examined.

Hydrochlorate of Strychnine.—This salt is formed by dissolving strychnine in hydrochloric acid. Two crystallizations from water render it perfectly pure. It is neutral to test paper.

I. 0·2701 grm of substance gave:
0·6704 „ „ carbonic acid and
0·1614 „ „ water.
II. 0·3351 „ „ substance gave:
0·8349 „ „ carbonic acid and
0·1881 „ „ water.
III. 0·5912 „ „ substance gave:
0·2280 „ „ chloride of silver.
IV. 0·1733 „ „ substance gave:
0·0671 „ „ chloride of silver.
V. 0·6060 „ „ substance exposed in an air-bath to a temperature of 120^0 lost
0·0445 „ „ water.
VI. 0·3985 „ „ exposed to the same temperature lost
0·0280 „ „ water.

which numbers correspond to the following per-centage composition:

	I.	II.	III.	IV.	V.	VI.
Carbon. .	67·69	67·95	—	—	—	—
Hydrogen .	6·63	6·23	—	—	—	—
Chlorine .	—	—	9·54	9·57	—	—
Water . .	—	—	—	—	7·33	7·02

leading to the formula,

$$C_{42}\,H_{22}\,N_2\,O_4,\ H\,Cl,$$

for the salt dried at 100° C. and for the crystallized salt:

$$C_{42}\,H_{22}\,N_2\,O_4,\ H\,Cl + 3\ aq.$$

as may be seen by the following comparison, to which we annex the results obtained by Regnault* and Gerhardt.†

	Theory.		A. & N. Mean.	Regnault.	Gerhardt.
42 equiv. of Carbon . .	252·00	68·01	67·82	67·82	65·08
23 „ „ Hydrogen .	23·00	6·20	6·43	6·75	6·94
2 „ „ Nitrogen. .	28·00	7·56	—	—	—
4 „ „ Oxygen . .	32·00	8·65	—	—	—
1 „ „ Chlorine. .	35·50	9·58	9·55	9·81	—
1 „ „ Hydrochlorate of strychnine . .	370·50	100·00			
3 „ „ Water . .	27·00	6·79	7·17	—	—
1 equiv. of crystallized salt	397·50				

Gerhardt has also determined the amount of water in this salt, and finds that it contains two atoms, which are only expelled on exposing the salt to a temperature of 160° C. Contrary to this statement we have found this salt, as well as the hydriodate, hydrobromate, sulphates and phosphates, to lose the whole of their water of crystallization on exposure over sulphuric acid *in vacuo.*

Hydrobromate of strychnine, produced by dissolving strychnine in hydrobromic acid, and crystallizing from water:

I. 0·2288 grm. of substance gave:
0·5104 „ „ carbonic acid, and
0·1154 „ „ water.
II. 0·6248 „ „ substance yielded:
0·2802 „ „ bromide of silver.

In 100 parts:

	I.	II.
Carbon	60·83	—
Hydrogen . . .	5·60	—
Bromine	—	18·69

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* Liebig's Annalen, V. 26, P. 30.

† Recherches sur la Classification Chimique, etc., par M. Gerhardt, p. 51.

leading to the formula:

$$C_{42}\, H_{23}\, N_2\, O_4\, H\, Br,$$

as is seen by the following comparison:

	Theory.		Expt.
42 equiv of Carbon	252·00	60·97	60·83
23 „ „ Hydrogen	23·00	5·56	5·60
2 „ „ Nitrogen	28·00	6·78	—
4 „ „ Oxygen	32·00	7·76	—
1 „ „ Bromine	78·26	18·93	18·69
1 „ „ Hydrobromate of strychnine	413.26	100·00	

Hydriodate of strychnine is prepared in a similar manner to the hydrochlorate. This is one of the most insoluble salts of strychnine. In purifying it, the excess of hydriodic acid should be rapidly removed by washing, otherwise, when the salt is exposed to the air, products of decomposition are formed, which we shall notice in our future communication.

I. 0·3269 grm. of substance gave:
0·6546 „ „ carbonic acid, and
0·1482 „ „ water.
II. 0·3294 „ „ substance gave:
0·6595 „ „ carbonic acid, and
0·1489 „ „ water.
III. 0·4736 „ „ substance gave:
0·2396 „ „ iodide of silver.
IV. 0·3576 „ „ substance gave:
0·1808 „ „ iodide of silver.

Per-centages obtained:

	I.	II.	III.	IV.
Carbon . . .	54·61	54·60	—	—
Hydrogen . .	5·03	5·02	—	—
Iodine . . .	—	—	27·00	27·24

agreeing with the formula:

$$C_{42}\, H_{22}\, N_2\, O_4,\, H\, I$$

as is shown by the following comparison (together with Regnault's analysis of this salt):

	Theory.		A. & N. mean.	Regnault.
42 equivs. of Carbon . .	252·00	54·62	54·60	55·08
23 „ „ Hydrogen .	23·00	4·98	5·02	—
2 „ „ Nitrogen .	28·00	6·07	—	—
4 „ „ Oxygen . .	32·00	6·95	—	—
1 „ „ Iodine . .	126·36	27·38	27·12	26·12
1 „ „ Hydriodate of strychnine	461.36	100·00		

Hydrosulphocyanate of strychnine.—This salt has recently been described in a memoir by Dollfus*, who, at the instigation of Professor Will, availed himself of the insolubility of sulphocyanide of silver for the determination of the equivalents of several organic bases; we have likewise investigated this salt. Our analyses made with two different specimens, slightly differ from the results obtained by Dollfus; the equivalent, derived from our determinations, of the hydrosulphocyanic acid, nearly coincides with the calculated number.

Strychnine being very difficultly soluble in water, a direct determination was made of it in this salt; by precipitating with ammonia, collecting on a tared filter, washing and drying at 100° C., a tolerably accurate result was obtained. We availed ourselves of this method in the analysis of several other salts of strychnine.

Analysis of the hydrosulphocyanate:

I. 0·3704 grm. of substance gave:
0·9090 „ „ carbonic acid, and
0·1975 „ „ water.
II. 0·2398 „ „ substance gave:
0·1013 „ „ sulphocyanide of silver.
III. 0·5377 „ „ substance gave:
0·2260 „ „ sulphocyanide of silver.
0·4563 „ „ strychnine.

In 100 parts:

	I.	II.	III.
Carbon	66·93	—	—
Hydrogen	5·92	—	—
Hydrosulphocyanic acid	—	15·90	14·93
Strychnine	—	—	84·86

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* Liebig's Annalen, Vol. LXV. p. 212.

Corresponding to the formula:

$$C_{42}\,H_{22}\,N_2\,O_4,\;H\,Cy\,S_2$$

as may be seen by the following comparison, which is accompanied by the numbers obtained by Dollfus:

	Theory.		A. & N.	Dollfus.
44 equivs. of Carbon	264	67·17	66·93	67·70
23 „ „ Hydrogen	23	5·85	5·92	6·39
3 „ „ Nitrogen	42	10·68	—	—
4 „ „ Oxygen	32	8·15	—	—
2 „ „ Sulphur	32	8·15	—	—
1 „ „ Hydrosulphocyanate of strychnine .	393	100·00		

	Theory.		A. & N.	Dollfus.
1 equiv of Strychnine	334	84·98	84·86	—
1 „ „ Hydrosulphocyanic acid	59	15·02	14·96	14·45
	393	100·00	99·92	

The equivalent of strychnine derived from the above analyses, is as follows:

	I.	II.
Equivalent deduced from the determination of hydrosulphocyanic acid	334·3	336·1
Mean	335·7	
Theoretical equivalent	334·0	

Neutral sulphate of strychnine.—This salt is prepared by saturating dilute sulphuric acid with finely powdered strychnine, it crystallizes in large four-sided prisms, which are neutral to test-paper.

I. 0·2905 grm. of substance gave:
0·6996 „ „ carbonic acid, and
0·1615 „ „ water.
II. 0·3889 „ „ substance gave:
0·1184 „ „ sulphate of baryta.

Per-centage obtained:

	I.	II.
Carbon	65·68	—
Hydrogen	6·17	—
Hydrate of sulphuric acid . .	—	12·79

These numbers correspond to the formula:

$$C_{42}\,H_{22}\,N_2\,O_4,\ H\,SO_4$$

as is seen by the following comparison, to which we append Regnault's* analysis of this salt:

	Theory.		A. & N.	Regnault.
42 equiv. of Carbon	252	65·80	65·68	65·34
23 „ „ Hydrogen	23	6·01	6·17	6·10
2 „ „ Nitrogen	28	7·31	—	—
8 „ „ Oxygen	64	16·71	—	—
1 „ „ Sulphur	16	4·17	—	—
1 „ „ Neutral sulphate of strychnine	383	100·00		

	Theory.		Experiment.
1 equiv. of Strychnine	334	87·22	—
1 „ „ Hydrated sulphuric acid	49	12·78	12·79
	383	100·00	

Acid sulphate of strychnine is formed by adding diluted sulphuric acid to the preceding salt; it crystallizes in long thin needles and is very acid to test-paper. The analyses were made with material from two different preparations:

I. 0·3589 grm. of sulphate yielded:
0·7729 „ „ carbonic acid, and
0·1885 „ „ water.
II. 0·3071 „ „ substance gave:
0·1642 „ „ sulphate of baryta.

In 100 parts:

	I.	II.
Carbon	58·73	—
Hydrogen	5·83	—
Hydrate of sulphuric acid	—	22·46

The following comparison shows this salt to correspond to the formula,

$$C_{42}\,H_{22}\,N_2\,O_4,\ H\,SO_4,\ H\,SO_4$$

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* Liebig's Annalen, Vol. XXVI. p. 33.

	Theory.		Expt.
42 equivs. of Carbon	252	58·33	58·73
24 „ „ Hydrogen	24	5·56	5·83
2 „ „ Nitrogen	28	6·48	—
12 „ „ Oxygen	96	22·22	—
2 „ „ Sulphur	22	7·41	—
1 equiv. of Acid sulphate of strychnine	432	100·00	—

	Theory.		Experiment.
1 equiv. of Strychnine	334	77·30	—
2 equivs. of Hydrated sulphuric acid	98	22·70	22·46
	432	100·00	

The small excess of carbon and hydrogen, and the deficiency of sulphuric acid in the above analyses, arises from the presence of a little neutral sulphate in the substance employed for the determinations, it being exceedingly difficult to separate this salt completely from the acid sulphate.

Nitrate of strychnine.—On gently heating finely powdered strychnine in nitric acid, diluted until it is but feebly acid to the taste, the base is dissolved; the solution, while cooling, deposits beautiful colourless needles of nitrate of strychnine. If the nitric acid be employed too concentrated, the solution assumes a yellow colour immediately on the application of heat, and the compound produced is no longer a salt of strychnine, but the nitrate of a base containing the elements of hyponitric acid in place of hydrogen, which we shall more minutely describe hereafter. The existence of an acid nitrate of strychnine is mentioned in "Liebig's Traité de Chimie Organique," we have not been able to prepare this compound; it is very probable that the formation of the nitro-base just mentioned, has given rise to the assumption of an acid nitrate.

0·3168 grm. of this salt gave, on combustion,
0·7365 „ „ carbonic acid, and
0·1668 „ „ water

in 100 parts:

Carbon	63·40
Hydrogen	5·85

corresponding to the formula,

$$C_{42}\,H_{22}\,N_2\,O_4,\ H\,NO_6,$$

as may be seen from the following comparison, annexed to which we give an analysis of this salt by Regnault*:

	Theory.		A. & N.	Regnault.
42 equivs. of Carbon	252	63·47	63·40	63·10
23 „ „ Hydrogen	23	3·79	5·85	5·89
3 „ „ Nitrogen	42	10·38	—	—
10 „ „ Oxygen	80	20·16	—	—
1 equiv. of Nitrate of strychnine	397	100·00		

Chromate of strychnine is formed as a yellowish-brown precipitate when a solution of neutral chromate of potash is added to hydrochlorate of strychnine. The precipitate, freed from the mother-liquor, is soluble in boiling water; on cooling the solution deposits the salt in beautiful lemon-yellow needles, which are difficultly soluble in water and alcohol, neutral to test-paper and may be dried at 100° C. (212° F.). A bichromate also exists; we have not, however, submitted it to analysis:

0·3037 grm. of chromate gave:
0·0613 „ „ sesquioxide of chromium.

corresponding to

Hydrate of chromic acid 15·34 per cent,

which, by comparison with the theoretical numbers, will lead to the formula,

$$C_{42} H_{22} N_2 O_4, H Cr O_4$$

	Theory.		Expt.
1 equiv. of Strychnine	334·00	84·53	—
1 „ „ Hydrate of chromic acid	61·15	15·47	15·34
1 equiv. of Chromate of strychnine	395·15	100·00	

Neutral oxalate of strychnine.—This salt is produced by neutralizing oxalic acid with strychnine, it is neutral to test-paper:

0·4731 grm. of substance gave by the method above described:
0·4162 „ „ strychnine:
0·0624 „ „ carbonate of lime.

equal in 100 parts to

Strychnine	87·98
Hydrate of oxalic acid	11·86

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* Liebig's Annalen, Vol. XXVI. p. 35.

leading to the formula:

$$C_{42}\,H_{22}\,N_2\,O_4,\ H\,C_2\,O_4$$

as a comparison with the theoretical numbers shows:

	Theory.		Experiment.
1 equiv. of Strychnine . . .	334	88·13	87·98
1 ,, ,, Hydrate of oxalic acid .	45	11·87	11·86
1 equiv. of neutral oxalate of strychnine	379	100·00	

Acid oxalate of strychnine.—An excess of oxalic acid, added to the preceding salt, yields this substance which is possessed of an acid reaction:

0·2610 grm. of substance gave:
0·2054 ,, ,, strychnine, and
0·0604 ,, ,, of carbonate of lime.

affording on 100 parts:

Strychnine . . .	78·69
Hydrate of oxalic acid .	20·82

The following comparison proves the correct formula for this salt to be

$$C_{42}\,H_{22}\,N_2\,O_4,\ HC_2\,O_4,\ HC_2\,O_4$$

	Theory.		Experiment
1 equiv. of Strychnine	334	78·77	78·69
2 equivs. of Hydrate of oxalic acid .	90	21·23	20·82
1 equiv. of acid oxalate of strychnine	424	100·00	

Acid tartrate of strychnine.—On dissolving strychnine in excess of tartaric acid, this compound is formed, crystallizing in needles which are acid to test-paper.

I. 0·4225 grm. of substance gave:
0·2904 ,, ,, strychnine, or 68·73 per cent.
II. 0·2222 ,, ,, substance gave:
0·1527 ,, ,, strychnine, or 68·74 per cent.

these numbers lead to the formula,

$$C_{42}\,H_{22}\,N_2\,O_4,\ H_2\,C_8\,H_4\,O_{12}$$

which will be found, on comparison, to correspond sufficiently with the theoretical per-centage:

	Theory		Mean.
1 equiv. of Strychnine . .	334	69·00	68·735
1 „ „ Hydrate of tartaric acid	150	31·00	—
1 equiv. of acid tartrate of strychnine	484	100·00	

Neutral tartrate of strychnine is formed by dissolving strychnine in a solution of the above salt. It is neutral to test-paper.

0·4416 grm. of substance yielded :
0·3595 „ „ strychnine, or 81·40 per cent. leading to the formula,

$$2\ (C_{42}\,H_{22}\,N_2\,O_4)\ H_2\,C_8\,H_4\,O_{12}$$

as is seen by the following comparison :

	Theory.		Experiment.
2 equivs. of Strychnine . .	668	81·66	81·40
1 equiv. of Hydrate of tartaric acid	150	18·34	—
1 equiv. neutral tartrate of strychnine	818	100·00	

We endeavoured to form a compound of potash, strychnine, and tartaric acid, by boiling strychnine in an aqueous solution of acid tartrate of potash, we found, however, that no double salt was formed, but that the results were neutral tartrate of potash, and acid tartrate of strychnine, as may be seen by the following equation:

$$2\ (K\ H\ T) + C_{42}\,H_{22}\,N_2\,O_4 = K_2,\overline{T} + (H, C_{42}\,H_{22}\,N_2\,O_4)\ H, \overline{T}.$$

The numbers mentioned under II. at the acid tartrate of strychnine, refer to a salt procured in this manner.

Hydrochlorate of strychnine and bichloride of platinum.—This compound is produced by the addition of bichloride of platinum to a solution of strychnine in hydrochloric acid as a yellowish-white precipitate nearly insoluble in water and ether, and difficultly soluble in boiling dilute spirit, from which solution it crystallizes in beautiful plates similar in appearance to mosaic gold.

This compound is soluble in concentrated nitric acid, giving rise to a new platinum salt, which we shall hereafter refer to. The following determinations were all made with material from different preparations, and dried at 100° C. (212° F.), at which temperature this compound retains no water.

I. 0·2850 grm of substance gave:
0·4874 „ „ carbonic acid, and
0·1157 „ „ water.

II. 0·4204 grm. of substance gave:
0·7205 „ „ carbonic acid, and
0·1660 „ „ water.
III. 0·7252 „ „ substance gave:
0·1312 „ „ platinum.
IV. 0·6854 „ „ substance gave:
0·1244 „ „ platinum.
V. 0·6053 „ „ substance gave:
0·1100 „ „ platinum.
VI. 0·4918 „ „ substance gave:
0·0897 „ „ platinum.
VII. 0·5084 „ „ substance gave:
0·0918 „ „ platinum.
VIII. 0·7479 „ „ substance gave:
0·1365 „ „ platinum.
IX. 0·3122 „ „ substance gave:
0·0567 „ „ platinum.
X. 0·3146 „ „ substance gave:
0·0573 „ „ platinum.
XI. 0·4432 „ „ substance gave:
0·0809 „ „ platinum.
XII. 1·1571 „ „ substance gave:
0·2104 „ „ platinum.

Per-centage composition.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.
C.	46·64	46·72	—	—	—	—	—	—	—	—	—	—
H.	4·51	4·22	—	—	—	—	—	—	—	—	—	—
Pt.	—	—	18·09	18·15	18·16	18·23	18·05	18·22	18.16	18·21	18.25	18·18

leading to the formula:

$$C_{42}\ H_{22}\ N_2\ O_4\ HCl,\ PtCl_2$$

as may be seen from the following comparison with the theoretical numbers, to which we append the analyses of Liebig* and Gerhardt:†

	Theory.		A. & N. Mean.	Mean Liebig.	Gerhardt.
42 equivs. of Carbon . .	252·00	46·65	46·69	—	—
23 „ „ Hydrogen .	23·00	4·26	4·44	—	—
2 „ „ Nitrogen .	28·00	5·18	—	—	—
4 „ „ Oxygen . .	32·00	5·93	—	—	—
3 „ „ Chlorine .	106·50	19·72	—	—	—
1 equiv. „ Platinum .	98·68	18·26	18·16	17·84	17·85
1 equiv. of hydrochlorate of strychnine and bichloride of platinum	540·18	100·00			

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* Liebig's Annalen, v. 26, p. 57.

† Classification Chimique des Substances Organiques, par M. Gerhardt, p. 51.

Liebig's beautiful method of determining the equivalents of organic bases from the double compounds of the hydrochlorates with bichloride of platinum, is the most precise and elegant mode that could possibly have been imagined. The analysis, nevertheless, if not conducted with sufficient care, may give rise to an erroneous expression. When only two or three hundred milligrammes of substance are at the experimentor's command, an error of 1 or 2 milligrammes in the weight of the metal will give rise to a difference of from four to six tenths of a per-cent, which must materially affect the formula for the substance. In three determinations, made by Liebig, we perceive a difference of four tenths of a per-cent; in two cases he obtained 17·7, and in the third 18·1 per cent.; the latter determination agrees exactly with the average of our ten determinations, which oscillate between 18·05 and 18·2. Gerhardt's determination of the platinum is more concordant with Liebig's lower ones.

Hydrochlorate of strychnine and terchloride of gold.—On adding terchloride of gold to a solution of hydrochlorate of strychnine, a voluminous bright yellow precipitate of the double salt is formed; it is purified by washing rapidly with cold water, and crystallizing from alcohol. When boiled with water, this compound undergoes decomposition, metallic gold separating. The compound is deposited from an alcoholic solution, in light orange-coloured crystals, which may be dried at 100^0 without decomposition.

I. 0·3102 grm. of substance gave on combustion:
0·4246 „ „ carbonic acid and
0·0995 „ „ water.

II. 0 3756 „ „ substance gave:
0·1095 „ „ gold.

III. 0·1516 „ „ substance gave:
0·0441 „ „ gold.

IV. 0·4334 „ „ substance gave:
0·1266 „ „ gold.

n 100 parts:

	I.	II.	III.	IV.
Carbon	37·33	—	—	—
Hydrogen . .	3·55	—	—	—
Gold	—	29·15	29·09	29·21

corresponding to the formula,

$$C_{42}\,H_{22}\,N_2\,O_4,\ HCl,\ AuCl_3$$

as the following comparison will show:

	Theory.		Experiment.
42 equivs. of Carbon	252·00	37.41	37·33
23 ,, ,, Hydrogen	23·00	3·42	3·42
2 ,, ,, Nitrogen	28·00	4·15	—
4 ,, ,, Oxygen	32·00	4·75	—
4 ,, ,, Chlorine	142·00	21·08	—
1 equiv. of Gold	196·66	29·19	29·15
1 ,, ,, Hydrochlorate of strychnine and ter-chloride of gold	673·66	100·000	

Hydrochlorate of strychnine and protochloride of palladium is precipitated as a brown flocculent mass, when protochloride of palladium is added to a solution of strychnine in hydrochloric acid. It is soluble in water and alcohol, from boiling solutions of which it crystallizes on their cooling in dark brown needles. It may be dried at 100° C. (212° F.) without decomposition, and affords metallic palladium when exposed to a high temperature.

I. 0·4437 grm. of substance gave :
0·0512 ,, ,, palladium.
II. 0·3121 ,, ,, substance gave :
0·0358 ,, ,, palladium.

Per-centage obtained,

	I.	II.
Palladium	11·50	11.47

agreeing with the formula,

$$C_{42} H_{22} N_2 O_4 HCl, PdCl.$$

as is shown by the following comparison :

	Theory.		Mean of Expt.
42 equivs. of Carbon	252·00	54·87	—
23 ,, ,, Hydrogen	23·00	5·01	—
2 ,, ,, Nitrogen	28·00	6.08	—
4 ,, ,, Oxygen	32·00	7·00	—
2 ,, ,, Chlorine	71·00	15·45	—
1 equiv. of Palladium	53·27	11·59	11·50
1 ,, ,, Hydrochlorate of strychnine and protochloride of palladium	459.27	100.00	

Strychine and protochloride of mercury.—If a solution of strychnine in dilute alcohol be added to an excess of protochloride of mercury, a white crystalline precipitate is immediately formed, which is insoluble in water, alcohol and ether, it may therefore be easily purified by washing. This compound, as well as the following, was burnt with chromate of lead in a combustion-tube provided with an elongated bulb as described by one of us in the analysis of the double compound of caffeine and protochloride of mercury,* carbonic acid, water and mercury being determined in one combustion.

I. 0·4815 grm. of substance gave:
0·7330 „ „ carbonic acid,
0.1636 „ „ water and
0.1595 „ „ mercury.
II. 0·4360 „ „ substance gave:
0 2070 „ „ chloride of silver, or
0·0512 „ „ chlorine.

in 100 parts,

	I.	II.
Carbon . . .	41·52	—
Hydrogen . .	3.77	—
Mercury . . .	33·12	—
Chlorine . . .	—	11.74

The following comparison of these results with the theoretical numbers shows this compound to have the formula,

$$C_{42} H_{22} N_2 O_4, 2 HgCl$$

	Theory.		Expt.
42 equivs. of Carbon	252·00	41·64	41·52
22 „ „ Hydrogen	22·00	3·63	3·77
2 „ „ Nitrogen	28·00	4·63	—
4 „ „ Oxygen	32·00	5·29	—
2 „ „ Chlorine	71·00	11·73	11·74
2 „ „ Mercury	200·14	33·08	33·12
1 equiv. of Strychnine and protochloride of mercury	605·14	100·000	

The substance therefore is analogous in composition to the aniline and leucoline compounds described by Professor Hofmann. It is soluble in dilute acids.

Sulphate of strychnine and protochloride of mercury.—The solution of the above compound in sulphuric acid yields a substance which is indistinctly crystalline, but of perfectly definite nature, consisting of the original body combined with one equivalent of sulphuric acid, its formula being

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* Mem. Chem. Soc. London, Vol. III. p. 321.

$$C_{42}\,H_{22}\,N_2\,O_4\,H\,SO_4,\,2\,Hg\,Cl$$

as the following determination shows, when compared with the theoretical numbers:

0·2535 grm. of substance gave:
0·0439 „ „ sulphate of baryta

corresponding to 7·27 per cent of hydrate of sulphuric acid.

	Theory.		Expt.
1 equiv of Strychnine	334·00	51·09	—
1 „ „ Hydrate of sulphuric acid .	49·00	7·49	7·27
2 equivs. of Chlorine	11·00	10·85	—
2 „ „ Mercury	200·14	30·57	—
1 equiv. of Sulphate of strychnine and protochloride of mercury	654·14	100·00	

Hydrochlorate of strychnine and protochloride of mercury is prepared by dissolving the above compound in hydrochloric acid, or by adding a solution of protochloride of mercury to hydrochlorate of strychnine. It is difficultly soluble in water, but easily so in spirit, crystallizing from boiling solutions on cooling.

I. 0·4968 grm. of substance gave:
0·7175 „ „ carbonic acid,
0·1735 „ „ water, and
0·1559 „ „ mercury.
II. 0·2990 „ „ substance gave:
0·2007 „ „ chloride of silver, or
0·0496 „ „ chlorine.

In 100 parts,

	I.	II.
Carbon	89·38	—
Hydrogen	3·88	—
Mercury	31·38	—
Chlorine	—	16·59

leading to the formula,

$$C_{42}\,H_{22}\,N_2\,O_4,\,H\,Cl,\,2\,Hg\,Cl$$

as is seen by the following comparison:

	Theory.		Expt.
42 equivs. of Carbon	252·00	39·27	39·38
23 ,, ,, Hydrogen	23·00	3·58	3·88
2 ,, ,, Nitrogen	28·00	4·36	—
4 ,, ,, Oxygen	32·00	4·98	—
3 ,, ,, Chlorine	106·50	16·61	16·59
2 ,, ,, Mercury	200·14	31·20	31·38
1 equiv. of Hydrochlorate of strychnine and protochloride of mercury	641·64	100·00	

The solutions of the two latter compounds give with ammonia a white precipitate. It appeared not improbable that under these circumstances a new basic atom, containing both strychnine and protochloride of mercury was thrown down. To ascertain this, a platinum-salt of the above precipitate was prepared and submitted to analysis. This salt gave 18·1 per cent. of platinum, proving that the precipitate was nothing but strychnine. The mercury in this instance was not precipitated as chloro-amidide of mercury, but held in solution as the double compound of chloride of ammonium and protochloride of mercury, $Hg\ Cl, N\ H_4\ Cl$.

Strychnine and cyanide of mercury.—This substance is produced in the same manner as the compound of strychnine with protochloride of mercury; it is more soluble in water and alcohol than the latter, and crystallizes in well defined small prisms. It is insoluble in ether, and may be dried at 100° C. (212° F.) without decomposition.

0·4098 grm. of substance gave:
0·7055 ,, ,, carbonic acid,
0·1395 ,, ,, water, and
0·1400 ,, ,, mercury.

In 100 parts:

Carbon	46·96
Hydrogen	3·78
Mercury	34·16

The following comparison shows this compound to have the formula,

$$C_{42}\ H_{22}\ N_2\ O_4,\ 2\ Hg\ Cy$$

	Theory.		Experiment.
46 equivs. of Carbon . .	276·00	47·08	46·96
22 „ „ Hydrogen .	22·00	3·75	3·78
4 „ „ Nitrogen . .	56·00	9·59	—
4 „ „ Oxygen . .	32·00	5·46	—
2 „ „ Mercury . .	200·14	34·12	34·16
1 equiv. of Strychnine and Cyanide of Mercury	586·14	100·00	

Hydrochlorate of strychnine and cyanide of mercury.—Brandes* has described a compound, produced by mixing solutions of hydrochlorate of strychnine and cyanide of mercury, the analysis of which led to the formula:

$$C_{44} H_{24} N_2 O_4 HCl, 4 Hg Cy.$$

We prepared a compound of this nature, according to the method described by the above chemist, and submitted it to analysis.

0·4356 grm. of substance gave:
0·8390 „ „ carbonic acid, and
0·0881 „ „ mercury.

In 100 parts:

Carbon . . .	52·53
Mercury . . .	20·20

These numbers agree with the formula:

$$C_{42} H_{22} N_2 O_4 HCl, Hg Cy$$

as expressive of the composition of this salt, as may be seen by comparison with the theoretical numbers,

	Theory.		Experiment.
44 equivs. of Carbon . . .	264·00	53·16	52·53
23 „ „ Hydrogen . .	23·00	4·63	—
3 „ „ Nitrogen . .	44·00	8·46	—
4 „ „ Oxygen . . .	32·00	6·45	—
1 equiv. „ Chlorine. . .	35·50	7·15	—
1 „ „ Mercury. . .	100·07	20·15	20·20
1 equiv. of Hydrochlorate of Strychnine and Cyanide of Mercury	496·57	100·00	

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* Liebig's Annalen, v. 66, p. 268.

It is probable from this that strychnine combines in various proportions with cyanide of mercury.

Besides the above compounds of strychnine, we have also examined its combinations with phosphoric and arsenic acids, which have furnished us peculiar results, especially the compound with metaphosphoric acid; we shall give a detailed description of these compounds in a separate paper.

Strychnine, likewise, forms difficultly soluble compounds with protochloride of platinum, protiodide and subnitrate of mercury, we have not submitted these salts to quantitative examination.

The following is a table of the compounds of strychnine analysed by us, with their formulæ annexed.

Strychnine	$C_{42}\ H_{22}\ N_2\ O_4$
Hydrochlorate of strychnine . .	$C_{42}\ H_{22}\ N_2\ O_4,\ HCl$
Hydrobromate ,, ,, . .	$C_{42}\ H_{22}\ N_2\ O_4,\ HBr$
Hydriodate ,, ,, . .	$C_{42}\ H_{22}\ N_2\ O_4,\ HJ$
Hydrosulphocyanate ,, . .	$C_{42}\ H_{22}\ N_2\ O_4,\ HCy\ S_2$
Neutral sulphate ,, ,, . .	$C_{42}\ H_{22}\ N_2\ O_4,\ HSO_4$
Acid sulphate ,, ,, . .	$C_{42}\ H_{22}\ N_2\ O_4,\ HSO_4,\ HSO_4$
Nitrate ,, ,, . .	$C_{42}\ H_{22}\ N_2\ O_4,\ HNO_6$
Chromate ,, ,, . .	$C_{42}\ H_{22}\ N_2\ O_4,\ HCr\ O_4$
Neutral oxalate ,, ,, . .	$C_{42}\ H_{22}\ N_2\ O_4,\ HC_2\ O_4$
Acid oxalate ,, ,, . .	$C_{42}\ H_{22}\ N_2\ O_4,\ HC_2\ O_4,\ HC_2,\ O_4$
Neutral tartrate ,, ,, .	$2\ (C_{42}\ H_{22}\ N_2\ O_4),\ H_2,\ C_8\ H_4\ O_{12}$
Acid tartrate ,, ,, . .	$C_{42}\ H_{22}\ N_2\ O_4,\ H_2\ C_8\ H_4\ O_{12}$
Hydrochlorate of strychnine and bichloride of platinum . . .	$C_{42}\ H_{22}\ N_2\ O_4,\ HCl,\ Pt\ Cl_2$
Hydrochlorate of strychnine and terchloride of gold	$C_{42}\ H_{22}\ N_2\ O_4,\ HCl,\ AuCl_3$
Hydrochlorate of strychnine and protochloride of palladium . . .	$C_{42}\ H_{22}\ N_2\ O_4,\ HCl,\ Pd\ Cl$
Strychnine and protochloride of mercury.	$C_{42}\ H_{22}\ N_2\ O_4,\ 2Hg\ Cl$
Sulphate of strychnine and protochloride of mercury	$C_{42}\ H_{22}\ N_2\ O_4,\ HSO_6,\ 2Hg\ Cl$
Hydrochlorate of strychnine and protochloride of mercury . . .	$C_{42}\ H_{22}\ N_2\ O_4,\ HCl,\ 2Hg\ Cl$
Strychnine and cyanide of mercury .	$C_{42}\ H_{22}\ N_2\ O_4,\ 2Hg\ Cy$
Hydrochlorate of strychnine and cyanide of mercury	$C_{42}\ H_{22}\ N_2\ O_4,\ HCl,\ Hg\ Cy$

The formula for strychnine arrived at by all these analyses is the same as that last proposed by Regnault,

$$C_{42}\ H_{22}\ N_2\ O_4$$

which has subsequently been translated by Gerhardt into the expression,

$$C_{44}\ H_{24}\ N_2\ O_4$$

the formula of late most generally adopted. The analyses made by Regnault, of the hydriodate, sulphate, and nitrate, all closely correspond with $C_{42}\ H_{22}\ N_2\ O_4$, as may be seen by referring to the analytical details. His determinations of carbon and hydrogen, in the base itself, are lower, however, than this formula will admit.

In conclusion, it may be mentioned, that the study of a series of products of substitution and decomposition, with which we have become acquainted in the course of these experiments, fully confirm the analyses of strychnine and its salts, so that we have no hesitation in adopting the formula:

$$C_{42} H_{22} N_2 O_4$$

as the true expression for this base.

The following Paper having been received subsequently to the last Meeting of the Society on June 18th, was ordered to be published by the Council.

XXVII.—*On the Isolation of the Organic Radicals.*

By E. Frankland.

Considering the importance of having positive proof of the existence of the hitherto hypothetical radicals entering, on the one hand, into the composition of the basic compounds of which alcohol is a type, and, on the other, giving rise to the acids of the series commencing with formic acid, it is somewhat remarkable that so few attempts have been made either to isolate these radicals, or at least to discover the simpler groups into which they are decomposed at the moment of their separation.

Although the method by which Bunsen* succeeded in isolating cacodyl, pointed out the conditions under which a similar separation of other radicals might be affected, yet, with the exception of an unsuccessful attempt made by Löwig to obtain ethyl, by the action of potassium upon chloride of ethyl, the subject does not seem to have received further attention until Kolbe† succeeded in isolating valyl (C_8 H_9) by an entirely different method, viz. by the electrolysis of valerianic acid.

The action of potassium upon cyanide of ethyl‡ induced me to hope, that by employing a body of less complex constitution, and a metal of a less electro-positive character, the radical might be separated without being at the same time broken up into the groups (C_2 H_2) and (C_2 H_3).

The weak affinity possessed by iodine for the organic groups, its energetic action upon metals, and the comparatively low temperature at which its organic compounds are decomposed with the separation of free iodine, suggested the combinations of this element as being well adapted for such experiments; and although, with the exception of potassium and sodium, probably no metal has any action upon these compounds at their ordinary boiling points, yet it appeared in the highest degree probable that, if the metal and iodide were exposed under pressure to a progressively increasing temperature, a point would be attained where the affinity of the metal for iodine overbalancing that of the radical for the same element, would determine the decomposition of the iodide. The nature of the products would, of course, depend greatly upon the temperature, and, perhaps, in some degree, upon the nature of the metal employed.

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* Annalen der Chemie, Bd. XLII. s 45.

† Memoirs and proceedings of the Chemical Society, vol. III. p. 285.

‡ Quarterly Journal of the Chemical Society, No. I. p. 60.

From the superior interest possessed by ethyl, I selected the iodide of that radical for my first experiments: the compound was prepared by placing 7 parts by weight of phosphorus into 35 parts of absolute alcohol, and adding, in small quantities at a time, 23 parts of iodine, the vessel being kept cool by immersion in ice-cold water; the liquid was then decanted from the sediment and distilled in a water-bath, the distillate twice washed with water, and allowed to stand for 24 hours over chloride of calcium, iodine having been previously added until the fluid remained permanently coloured; it was then distilled three times from chloride of calcium, mercury, and anhydrous oxide of lead: when thus purified, its boiling point, as indicated by a thermometer placed immediately above the liquid, was 71·6° C. (161° F.) at 746·5 m.m. pressure (29·39 English inches); with the bulb of the thermometer immersed in the fluid, the temperature remained constant at 72·2°C. (162° F.); its specific gravity, as indicated by a carefully conducted experiment, was 1·9464 at 16°C. (61° F.).

Burnt with oxide of copper,* 0·5618 grms. yielded 0·3190 grms. carbonic acid, and 0·1607 grms. water; numbers which indicate the following per-centage composition:

		Calculated.	Expt.
4 eqs. Carbon . . .	300	15·42	15·48
5 „ Hydrogen . .	62·5	3·20	3·18
1 eq. Iodine . . .	1585·5	81·38	
	1948·0	100·00	

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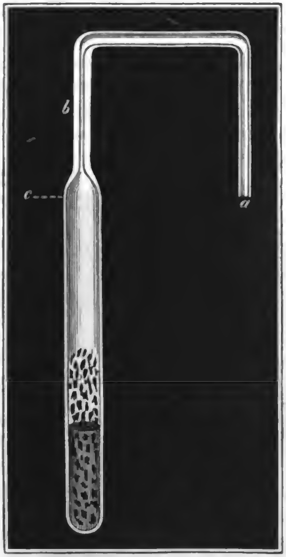
* In this analysis, about four inches of the front end of the combustion tube was filled with copper turnings and maintained at a heat just below visible redness during the whole operation. After the combustion, the liquid in the potash apparatus did not contain a trace of iodine

In order to subject this liquid, in contact with different metals, to temperatures considerably above its boiling point, and at the same time to preserve any gases that might be evolved, the following method was adopted: tubes of hard Bohemian glass, 1 cm. in diameter, the thickness of the glass being about 1·3 mm., were cut into lengths of 12 inches each, and carefully closed at one end before the blow-pipe so as not to diminish the thickness of the glass. The metals, either finely granulated, or otherwise treated so as to expose a large surface, were then introduced, and the open extremity of the tube was drawn out to the thickness of a straw; about an inch of this narrow tube, at *b* Fig. 1., was then brought into the hottest portion of the flame, and the glass allowed to shrink up until a fine capillary bore was obtained; the narrow tube was then bent twice at right angles as shewn in the figure. The whole being now warmed, the open extremity (*a*) was immersed in the iodide of ethyl, which, by the subsequent contraction of the enclosed air, was forced into the apparatus in the required quantity; the tube (*a*) being then connected with an air-pump by means of a strong caoutchouc joint, the apparatus was exhausted, and the tube finally hermetically sealed at (*b*): as the liquid boiled violently during the exhaustion, it was easy to effect the expulsion of the last traces of air. The tubes thus prepared were afterwards exposed to the necessary heat by immersing them to half their length in an oil-bath.

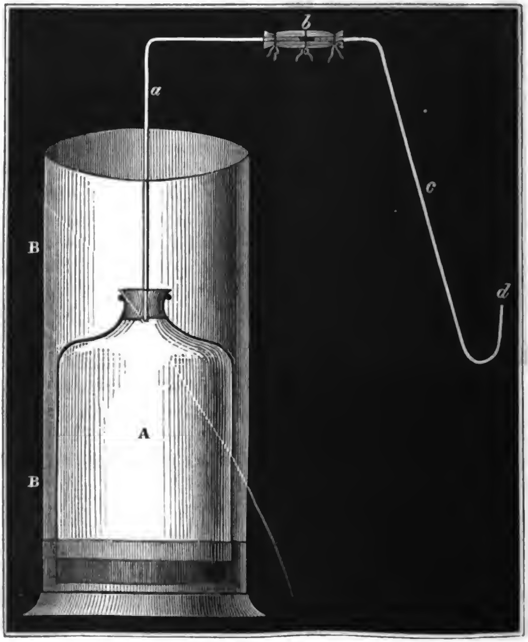
FIG. 1.



ACTION OF ZINC UPON IODIDE OF ETHYL.

A preliminary experiment, conducted as above described, shewed that the decomposition of iodide of ethyl, by zinc, commences at a temperature of about 150° C. (302° F.), and proceeds with tolerable rapidity when an extensive surface of the metal is exposed; white crystals gradually encrust the zinc and glass, whilst a colourless mobile liquid remains, equal in volume to only about half the iodide of ethyl employed, and very different from that liquid in appearance; it was further evident, from the cessation of ebullition soon after decomposition commenced, that a gas or highly elastic vapour had been generated. Having been maintained at the above temperature for about two hours, and the decomposition appearing to be complete, the tube was removed from the bath and allowed to cool. On, afterwards, breaking off its capillary extremity under water, about forty times its volume of gas was evolved, whilst the whole of the mobile fluid, above mentioned, disappeared; the gas had a strong ethereal odour, burnt with a bright flame, and was rapidly and completely absorbed by recently boiled absolute alcohol. On cutting off the upper portion

FIG. 2



of the tube, and introducing distilled water, the white mass of crystals dissolved with brisk effervescence, occasioned by the evolution of a considerable quantity of a gas possessing properties quite similar to those just mentioned. The solution of the crystals thus obtained possesses all the properties of a solution of iodide of zinc and, with the exception of a trace of undecomposed iodide of ethyl, appeared to contain no organic substance.

For the collection and preservation of the gas, I used the apparatus shown in Fig. 2. *A* is a bell jar, open below and passing easily into the cylinder *BB*, its upper orifice is closed by a sound cork, through which passes the glass tube (*a*), which is bent above at right angles, and connected by the caoutchouc joint (*b*) with the gas-delivering tube (*c*); within the joint (*b*), and between the tubes (*a*) and (*c*), is placed a piece of glass rod, half an inch in length, and rather smaller in diameter than the flexible tube, so that by means of an external ligature, the communication can be opened or closed at pleasure, without injury to the caoutchouc connector.

It was absolutely necessary to collect the gas over water, and to allow it to stand at least twenty-four hours, in order that the vapour of undecomposed iodide of ethyl might be perfectly absorbed: during this time a diffusion between the gas and atmospheric air is constantly going on, and cannot be wholly prevented even by a layer of oil; since, therefore, in the present case, it was found that the absorption of oxygen by phosphorus could only be effected at a temperature considerably above the fusing point of the latter, which would render the correct estimation of the oxygen a matter of considerable difficulty, it appeared desirable to prevent the ingress of every trace of oxygen. This object was easily and perfectly attained by mixing some alkaline solution of sulphuret of potassium with the water used in the pneumatic operations, thus the passage of this gas into the receiver was rendered impossible.

An earthen vessel of convenient size, and admitting of the total immersion of the cylinder *BB* being filled with this sulphuretted water, the bell glass *A*, having the valve (*b*) open, was pressed beneath its surface until the included atmospheric air had been completely expelled through the tubes (*a*) and (*c*), which also become filled with the fluid on suction being applied at the orifice (*d*); the valve at (*b*) being then securely closed, the apparatus was ready for the reception of the gas.

One of the decomposition tubes before mentioned, in which about six grammes of iodide of ethyl had been exposed to the action of zinc was now brought beneath the vessel *A*, and the capillary portion being cut through with a file, the compressed gas rushed into the receiver, at first with considerable violence, but afterwards in a slow stream, which did not entirely cease until after the lapse of nearly a quarter of an hour; the cylinder *BB*, filled with the prepared water, was now brought under the bell jar *A*, and the latter being lowered into it, both were removed from the large vessel: the gas, which I will call *α*, was then allowed to stand over the confining liquid for twenty-four hours before being used for further experiments.

After the lapse of twelve hours, the contracted portion of the tube from which the compressed gas had been evolved was cut off at *c* (Fig. 1), and a smaller bent tube and cork having been fitted to the orifice, distilled water was poured upon the residue, and the cork furnished with the gas-delivering tube immediately inserted; a rapid disengagement of gas ensued, which was allowed to escape until every trace of atmospheric air had been expelled; this gas, which I will call *β*, was then collected in a similar apparatus, and with like precautions to those used in the collection of *α*.

The gas *α* was first submitted to investigation; the determination of its specific gravity was made in a light glass flask capable of containing upwards of 200 cubic centimeters, and having a millimeter scale etched upon its neck; a few fragments of fused potash having been introduced into this flask, and fixed to the glass by being first moistened with water, and then gently heated, it was carefully filled with mercury, and inverted in a vessel containing the same metal. The apparatus *BB*, *A* being then conveniently arranged, the valve (*b*) was loosened, and the gas, acting under the external pressure, allowed to force out the water occupying the tubes (*a*) and (*c*) from the orifice (*d*), which had been previously immersed in quicksilver; as soon as the water had been completely expelled, and removed from the surface of the metal by blotting paper, the bent extremity of the tube (*c*) was introduced within the neck of the specific gravity flask, so that its orifice was somewhat above the level of the external mercury; by this last arrangement, the inconvenience of employing great pressure in *BB* to overcome that of the mercury was entirely avoided, an external column of water, a few inches in height, being sufficient to counteract the capillary action of the tubes. The gas was allowed to enter the flask until the external and internal mercury stood at the same level, and the tube (*c*) being removed, the rest of the gas in *A* was immediately transferred for eudiometrical analysis to a receiver standing over the mercury: a thermometer being now brought into the vicinity of the apparatus, the whole was allowed to remain for several hours in a room of constant temperature, until the moist gas became perfectly dried by the pieces of fused potash. The thermometer, barometer, and height of the internal column of mercury above that in the outer vessel, were then read off by means of a telescope placed at the distance of a few feet, and the flask, after being securely stopped without bringing the hand in contact with it, was weighed, afterwards filled with dry air, and lastly with quicksilver, the weight being taken in each case.

The following numbers were obtained:

Temperature of room	6·2°C.
Height of barometer	760·9mm.
Difference of mercury level	19·4mm.
Weight of flask and gas	54·6213 grms.
Temperature in balance case	7·8° C.
Weight of flask and air	54·4838 grms.
Temperature in balance case	8·0° C.
Capacity of flask	211·23 Cbc.
From which the sp. gr. was calculated to be	1·5250.

The composition of this and of the following gases, was determined by the eudiometrical processes of Professor Bunsen, by which the estimations can be made with a degree of accuracy previously unattainable in this branch of chemical research: I gladly avail myself of this opportunity to express my warmest thanks to that gentleman for the very kind manner in which he placed his laboratory, and especially the whole of his admirably arranged eudiometrical apparatus, at my disposal during the progress of this investigation.

The gas to be examined was transferred into a short eudiometer, and rendered perfectly dry by means of a ball of potash, the volume being then noted with the necessary precautions, a recently ignited coke bullet, saturated with very strongly fuming sulphuric acid, was introduced and allowed to remain in the gas until the volume of the latter ceased to diminish. After the removal of the coke bullet, the sulphurous, and vapours of anhydrous sulphuric acid, were removed by a ball of moist peroxide of manganese, and the gas being lastly dried by a ball of fused potash, its volume was again noted. After a specimen of the gas had been removed for combustion with oxygen, and the remaining volume once more read off, absolute alcohol, well-boiled and still warm was introduced by means of a bent pipette, agitated with the gas and allowed to stand for several hours; the remaining volume, after correction for the tension of alcohol vapour, was regarded as pure nitrogen.

The specimen of gas removed after absorbtion by sulphuric acid was transferred into a long eudiometer, furnished with platinum wires for the transmission of the electric spark, and, its volume being taken, was exploded with measured quantities of oxygen and atmospheric air;* the volume being again read off, a ball of fused potash was introduced and allowed to remain in the gas until every trace of carbonic acid was absorbed; on the subsequent removal of the potash ball and another determination of the volume, the remaining gas was exploded with a known quantity of hydrogen in excess, and the resulting contraction ascertained.

It is almost unnecessary to state that the observations were always made, either when the gases were perfectly dry or fully saturated with vapour. The corrections for temperature were calculated according to Marchand's Tables in which the expansion-coefficient for each degree of the centigrade scale is taken as = 0·003665. Regnault's table of the expansive force of aqueous vapour was used in correcting for moisture; and for alcohol vapour, the numbers given by Schmidt were employed.

The volume of combustible gas, brought into the large eudiometer was found by deducting from the first reading, the due proportion

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* The analysis of this gas presented some difficulties, its combustion in the usual manner with oxygen, produced such an intense explosion, that no ordinary eudiometer could resist its violence, the analysis was, therefore, conducted in a eudiometer 0·8 meter in length, and the gas, previous to combustion, was mixed with about 26 times its volume of atmospheric air, and 3 times its volume of oxygen, by this means, the violence of the explosion was moderated and, as shewn by Kolbe (Memoirs of the Chemical Society for 1846, p. 245), the oxydation of the nitrogen to nitric acid prevented; pure oxygen cannot be used for this purpose, since the excess required is too great to be afterwards determined by explosion with hydrogen, unless a eudiometer of inconvenient length be employed; this dilution, however, cannot be carried beyond a certain limit without interfering with the accuracy of the results, for when the explosion becomes exceedingly week, a portion of the carbon is oxidized to carbonic oxide, instead of carbonic acid, as is shewn by the following experiments in which the gas was exploded with different quantities of atmospheric air and oxygen.

	Vol. of gas.	Vol. of air and O.	O consumed.	CO_2 generated.
(I).	1	36·3	4·40	2·82
(II.)	1	32·4	5.28	3·17
(III.)	1	28·8	5·36	3·28
(IV.)	1	18·7	5·54	3·26

In experiments (I.) and (II.) the explosion was very slight, and the subsequent combustion with hydrogen indicated a larger quantity of nitrogen than was contained in the gas and atmospheric air, a result which could only have been produced by an imperfect combustion. In experiment (No. IV.), the heat developed by the explosion was so great, that a portion of the mercury was volatilized, covering the internal walls of the eudiometer with a black film, the greater part of which soon became converted into white crystals of nitrate of mercury.

of nitrogen as ascertained in the small eudiometer. The third and fifth readings, viz.: the determination of the volume after the admission of oxygen and after absorption of carbonic acid, together with the first reading, gave data for calculating the amount of oxygen consumed, independently of the composition of atmospheric air, the variations in which would have introduced not unimportant inaccuracies into the analyses, had its average composition been made an element in the calculation. If, therefore, we denote the volume of combustible gas by (c), the quantity of nitrogen and oxygen contained in the mixture at the third reading, by $(N+O)$ and the total volume of gas at the third reading by A, we obtain the following equation:

$$c+(N+O)=A.$$

Further, if we represent the volume at the fifth reading, viz.: the volume after absorption of carbonic acid, by B and the unknown volume of oxygen consumed, by x; then, as B contains all the nitrogen and oxygen originally contained in $(N+O)$ minus the volume of oxygen which has been consumed by the combustible gas, it is evident that

$$(N+O)=B+x.$$

If then we substitute the quantity $B+x$ for $(N+O)$ in the first equation, we obtain the expression

$$c+B+x=A.$$

And hence for x, the value

$$x=A-B-c.$$

The quantity of carbonic acid generated was obtained by substracting the fifth from the fourth reading, and finally the explosion of the remaining gas with hydrogen in excess, shewed whether or not perfect combustion had taken place; for if the gas remaining after the absorption of carbonic acid consisted only of oxygen and nitrogen then the quantity of the latter ought nearly to correspond with the amount introduced in the combustible gas and atmospheric air.

In none of the following analyses was the heat eliminated by combustion with excess of oxygen so great as to cause the volatilization of the quicksilver, the occurrence of which, when nitrogen is present, is always accompanied by the formation of nitric acid.

I.

	Observed vol.	Temp. C.	Difference of mercury level.	Barom.	Corrected vol. at 0° C. and 1_m pressure
Gas used (dry).	116·2	7·9°C.	14.9^{mm}	$738·8^{mm}$	81·75
After absorption by SO_3 (dry).	93·6	8·2°	30·5 „	735·1 „	64·03
After removal of specimen for combustion (dry.)	82·3	9·0°	42·3 „	735·3 „	55·21
After absorption by alcohol.	2·7	9·2°	42·8*	732·9 „	1·76

II.

Gas used (dry).	123·1	8·3°	6·1 „	741·3 „	87·83
After absorption by SO_3 (dry.	98·8	7·7°	24·0 „	739·4 „	68·74
After removal of specimen for combustion (dry).	87·8	8·2°	37·3 „	733·1 „	59·31
After absorption by alcohol	2·9	8·1°	56·5 „	734·8 „	1·86

III.

Gas used (moist).	102·2	8·4°	618·8 „	735·7 „	10·79
After admission of atmospheric air (moist).	543·7	8·6°	160·8 „	735·6 „	298·60
After admission of O. (moist).	569·1	8·7°	137·8 „	735·6 „	325·07
After combustion (moist).	537·5	8·7°	166·7 „	735·6 „	291·96
After absorption of CO_2 (dry).	498·0	8·6°	202·7 „	735·8 „	257·37
After admission of H (dry.)	626·9	9·0°	87·2 „	735·6 „	393·51
After combustion (moist).	549·6	9·0°	155·4 „	735·3 „	303·96

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* The pressure of the stratum of alcohol, resting upon the mercury within the eudiometer in this and the following analyses, is calculated into millimeters of quicksilver and added to the difference of mercury level.

IV.

	Observed vol.	Temp. C.	Difference of mercury level.	Barom^r.	Corrected vol. at 0° C. and 1^m pressure.
Gas used (moist).	104·0	8·3°	617·5^{mm}	737·0^{mm}	11·23
After admission of atmospheric air (moist).	538·3	8·3°	166·0 „	736·8 „	293·91
After admission of O. (moist).	577·0	8·0°	131·6 „	736·1 „	334·38
After combustion (moist).	544·3	7·9°	160·8 „	736·1 „	300·09
After absorption of CO_2 (dry).	505·2	7·6°	196·4 „	733·5 „	263·99
After admission of H (dry).	636·5	8·3°	79·1 „	733·1 „	403·98
After combustion (moist).	532·0	8·3°	171·8 „	732·2 „	285·10

According to analyses I. and II., the original gas contained in 100 parts:

	I.	II.	MEAN.
Gas absorbable by SO_3. . .	21·68	21·73	21·70
Gas unabsorbable by SO_3 . .	75·82	75·82	75·82
Nitrogen	2·50	2·45	2·48
	100·00	100·00	100·00

According to analyses III. and IV., the combustible gas, remaining after absorption by sulphuric acid, gave the following results:

	III.	IV.
Oxygen consumed by 1 vol.. . . .	5·48	5·47
Carbonic acid generated by 1 vol.. .	3·31	3·32

From the simple laws regulating the atomic volume of gaseous bodies, it is evident that no single gas could yield the results just given, it was also highly improbable that a gas having the general formula $C_n H_n$ could, after the action of fuming sulphuric acid, be present, since these gases so far as is at present known, are all rapidly absorbed by that acid; and as the absence of hydrogen and light carburetted hydrogen had been proved by the solubility of the gas in alcohol, the conclusion was almost unavoidable that the mixture consisted of methyl and the hitherto unisolated radical ethyl. It will be seen, from the following calculations, how far this supposition was borne out by the combined results of the eudiometrical and specific gravity experiments.

The estimation of the relative quantities of ethyl and methyl depends upon the circumstance, that ethyl consumes 6½ times its volume of oxygen, and generates 4 times its volume of carbonic acid, whilst methyl consumes 3½ volumes of oxygen, and generates 2 volumes of carbonic acid; but, as the volume of the mixed gases is known, we require only one other known quantity for the formation of two equations from which to determine the two unknown quantities; the contraction produced by the explosion of the gas with oxygen, and which is found by subtracting the fourth from the third reading, is a value in which both the oxygen consumed and carbonic acid generated are involved, and I have, therefore, made choice of this number for the second equation. As the quantity representing this contraction is compounded of the volume of combustible gas, *plus* oxygen consumed *minus* carbonic acid generated, it is clear that ethyl will produce a contraction equal to 3½ times its own volume, and methyl a contraction equal to 2½ times its volume. If, then, we represent the volume of combustible gas (obtained by subtracting the known amount of nitrogen from the observed volume) by A, the contraction produced during combustion by B, and the quantities of ethyl and methyl present, respectively by (x) and (y), we obtain the following equations:

$$x + y = A$$
$$\tfrac{7}{2}x + \tfrac{5}{2}y = B$$

Hence the values of x and y are:

$$x = \frac{2B - 5A}{2}$$
$$y = \frac{7A - 2B}{2}$$

According to analysis (No. III.), 10·79 vols. containing 0·34 vols. nitrogen, and 10·45 vols. of combustible gas, consumed 57·25 vols. oxygen, and generated 34·59 vols. carbonic acid, causing a contraction equal to 33·11 vols. By substituting the numbers here representing the volume of combustible gas, and the contraction, for A and B in the above equations, we obtain the following numerical values for x and y:

$$x = 6·98$$
$$y = 3·47$$

In analysis (IV.) 11·23 vols. containing 0·35 vols. nitrogen and 10·88 vols. of combustible gas, consumed 59·51 vols. oxygen and generated 36·10 vols. carbonic acid producing a contraction of 34·29 vols.; from which we obtain as the values of x and y:

$$x = 7{\cdot}09$$
$$y = 3{\cdot}79$$

Hence, the 75·82 per cent. of combustible gas, left unabsorbed by fuming sulphuric acid, contained on the above supposition:

	III.	IV.	MEAN.
Ethyl . .	50·64	49·41	50·03
Methyl . .	25·18	26·41	25·79
	75·82	75·82	75·82

In order to ascertain the composition and state of condensation of the gaseous body absorbed by fuming sulphuric acid, the original gas was exploded with atmospheric air and oxygen, precautions, exactly similar to those already described, being observed. The following numbers were obtained:

V.

	Observed vol.	Temp. C.	Difference of mercury level.	Barom^{r}.	Corrected vol. at 0° C. and 1^{m} pressure.
Gas used (moist).	99·6	7·4°	621·5^{mm}	735·9^{mm}	10·35
After admission of atmospheric air (moist.)	508·9	7·2°	192·4 „	735·8 „	265·66
After admission of oxygen (moist).	559·5	7·2°	146·0 „	735.8 „	317·37
After combustion (moist).	530·8	7·1°	172·0 „	736·1 „	287·95
After absorption of CO_2 (dry).	494·3	7·3°	206·8 „	741·3 „	253·72
After admission of H (dry).	701·3	7·3°	24·1 „	741·2 „	489·80
After combustion (moist).	563·3	7·3°	142·8 „	741·5 „	324·29

VI.

Gas used (moist).	108·1	9·2°	610·3 „	734·9 „	12·12
After admission of atmospheric air (moist).	533·7	9·2°	167·5 „	734·9 „	288·45
After admission of oxygen (moist).	589·9	9·0°	117·1 „	734·2 „	347·49

	Observed vol.	Temp. C.	Difference of mercury level.	Barom^r.	Corrected vol. at 0° C. and 1^m pressure.
After combustion (moist).	557·6	8·9°	146·6^{mm}	734·3^{mm}	312·76
After absorption of CO_2 (dry).	518·7	9·0°	181·2 „	733·1 „	277·13
After admission of H (dry).	706·3	9·0°	18·2 „	732·6 „	488·47
After combustion (moist).	558·0	8·8°	146·4 „	732·4 „	312·18

According to analysis (No. V.) 10·35 vols., containing 10·10 vols. of combustible gas, consumed 49·95 vols. oxygen, and generated 30·63 vols. carbonic acid; but 10·35 vols. of the original gas would contain, according to the mean of the analyses I. and II., 7·85 vols. of combustible gas unabsorbable by fuming sulphuric acid, which would consume (vide analyses III. and IV.) 43·02 vols. of oxygen, and generate 26·06 vols. carbonic acid; leaving 6·93 vols. oxygen and 4·57 vols. carbonic acid, as the oxygen consumed and carbonic acid generated by 2·25 vols. of the gas removed by fuming sulphuric acid.

Analysis (No. VI.) leads to a similar result, 12·12 vols., containing 11·82 vols. of combustible gas, consumed 58·54 vols. oxygen, and generated 35·63 vols. carbonic acid; and as this quantity of the original gas would contain 9·19 vols. of the mixture of ethyl and methyl, which would consume 50·36 vols. oxygen and generate 30·51 vols. carbonic acid, therefore, the remaining 2·63 vols. of gas absorbed by sulphuric acid consumed 8·29 vols. oxygen, and generated 5·00 vols. carbonic acid.

Hence the results yielded by the gas absorbable by sulphuric acid may be thus expressed:

	V.	VI.	MEAN.
Oxygen consumed by 1 vol. . . .	3·08	3·11	3·09
Carbonic acid generated by 1 vol.	2·03	1·95	1·99

The gas removed by sulphuric acid appears, therefore, to have exactly the composition and state of condensation possessed by elayl, 1 vol. of which requires, for its combustion, 3 vols. of oxygen, and generates 2 vols. of carbonic acid, numbers which sufficiently coincide with those just given, when we consider that any errors of observation are concentrated upon a small portion of the combustible gas.

To control this result, a quantity of the original gas, perfectly dried by passing over chloride of calcium, was allowed to stream through a

Liebig's potash apparatus containing perchloride of antimony, which rapidly combines with the gas absorbable by sulphuric acid, but has no action upon ethyl, as shewn below, or upon methyl. An indefinite quantity of the brown crystallizable liquid thus obtained was carefully burnt with oxide of copper, the front end of the combustion-tube being furnished with a layer of copper turnings. After the combustion, the weight of the potash apparatus was found to have increased by 0·1164 grms., and that of the chloride of calcium tube by 0·0473 grms. These numbers correspond with the following atomic proportion:

$$\begin{array}{l} C : H = 0{\cdot}0053 : 0{\cdot}0053 \\ C : H = 2 : 2 \end{array}$$

A result which completely confirms the eudiometrical analyses. Whether this body be really identical with elayl, or only isomeric with it, must be decided by further researches.

The per-centage composition of the gas *a* may, therefore, according to the mean of the foregoing analyses, be expressed as follows:

Elayl . . .	21·70
Ethyl . . .	50·03
Methyl . .	25·79
Nitrogen . .	2·48
	100·00

The theoretical specific gravity of a mixture possessing this composition, agrees closely with that found by experiment as is seen from the following simple calculation:

$$\begin{array}{lcrcrcr} C_2H_2 & = & 21{\cdot}70 & \times & 0{\cdot}96742 & = & 20{\cdot}9930 \\ C_2H_3 & = & 25{\cdot}79 & \times & 1{\cdot}03652 & = & 26{\cdot}7319 \\ C_4H_5 & = & 50{\cdot}03 & \times & 2{\cdot}00390 & = & 100{\cdot}3551 \\ N & = & 2{\cdot}48 & \times & 0{\cdot}96740 & = & 2{\cdot}3992 \\ \hline & & 100.00 & & & & \dfrac{150{\cdot}4792}{100} = 1{\cdot}504793 \end{array}$$

Specific gravity as found by experiment . . 1·5250

EXAMINATION OF THE GAS β.

This gas which occupies only about $\frac{1}{10}$ of the volume of the last, was treated in a similar manner: the eudiometrical experiments gave the following numbers:

I.

	Observed vol.	Temp. C.	Difference of mercury level.	Barom^r.	Corrected vol. at 0° C. and 1^m pressure.
Gas used (dry).	160·6	13·2°	$4·3^{mm}$	$737·8^{mm}$	112·37
After absorption by SO_3 (dry).	156·2	12.6°	8·7 „	741·7 „	109.44
After removal of specimen for combustion (dry).	128·8	13·9°	37·8 „	742·1 „	86.32
After absorption by alcohol.	8·2	14·0°	42·3 „	742·0 „	5·26

These numbers, reduced for 100 parts, give:

Gas absorbable by SO_3	2·61
Combustible gas unabsorbable by SO_3 . .	91·46
Nitrogen	5·93
	100·00

The combustion, with oxygen, of the gas remaining after treatment with fuming sulphuric acid, gave the following results:

II.

	Observed vol.	Temp. C.	Difference of mercury level.	Barom^r.	Corrected vol. at 0° C. and 1^m pressure.
Gas used (moist).	116·9	13·5°	$598·9^{mm}$	$741·8^{mm}$	14·64
After admission of atmospheric air (moist).	454·3	13·4°	240·8 „	741·8 „	211·97
After admission of O (moist).	540·2	13·5°	160·5 „	741·7 „	293·25
After combustion (moist).	502·0	13·4°	195·9 „	741·8 „	255·71
After absorption of CO_2 (dry).	463·8	13·3°	236·6 „	738·5 „	221·96
After admission of H (dry).	716·8	13·3°	13·7 „	738·4 „	495·32
After combustion (moist).	551·8	13·5°	154·9 „	738·8 „	300·96

III.

Gas used (moist).	121·2	13·6°	594·3 „	738·7 „	15·33
After admission of atmospheric air (moist).	448·0	13·7°	247·7 „	738·6 „	204·42

	Observed vol.	Temp. C.	Difference of mercury level.	Barom^{r}.	Corrected vol. at 0° C. and 1^{m} pressure.
After admission of O (moist).	529·4	14·0°	171·27^{mm}	39·3^{mm}	280·08
After explosion (moist).	488·0	14·3°	209·4 „	739·8 „	240·34
After absorption of CO_2 (dry).	440·9	13·5°	254·7 „	742·0 „	204·72
After admission of H (dry).	662·7	13·9°	52·2 „	742·1 „	435·04
After explosion (moist).	520·6	14·0°	178·0 „	742·2 „	273·49

According to analysis (No. II.) 14·64 vols., containing 13·75 vols. combustible gas, consumed 57·54 vols. oxygen, and generated 33·75 vols. carbonic acid, producing a contraction of 37·54 vols. In analysis (No. III.) 15·33 vols., containing 14.40 vols. combustible gas, consumed 60·96 vols. oxygen, and generated 35·62 vols. carbonic acid, suffering a diminution of volume during combustion equal to 39·74 vols.; numbers which correspond with the following proportions:

	Vol. of comb. gas.		O. consumed.		CO^2 generated.
II.	1	:	4·18	:	2.46
III.	1	:	4·23	:	2·47

From the behaviour of the gas with fuming sulphuric acid, and from the results of its combustion with oxygen, there can be no doubt that it is a mixture of the same ingredients as the gas *a*, the only difference being in the relative proportions of the two; and if we apply the formulæ before given, we obtain the annexed values for (x) and (y):

ANALYSIS NO. II.

$x = 3·17$
$y = 10·58$

ANALYSIS NO. III.

$x = 3.74$
$y = 10·66$

From which, omitting the nitrogen, we obtain the following percentage composition:

	I.	II.
Elayl	2·78	
Ethyl	22·41	25·25
Methyl	74·81	71·97
	100·00	

The determination of the atomic constitution of the crystalline body from which this gas is evolved, would be attended with great difficulty, as it is rapidly decomposed on coming in contact with the atmosphere, the crystals becoming almost instantaneously brown with the simultaneous production of an oxyiodide of zinc.

If, instead of allowing the tube to stand for twelve hours, as in the above instance, water be poured upon the residue immediately after the gas *a* has ceased to be evolved, the resulting gaseous mixture differs widely from that just described, in the relative proportions of ethyl and methyl composing it, as is shown by the following analysis of gas thus prepared and collected over mercury; the elayl, which was present only in small quantity, and the vapour of iodide of ethyl were removed by the introduction of a coke bullet saturated with fuming sulphuric acid, and the sulphurous acid, &c., by the subsequent insertion of a potash ball. The gas was perfectly absorbed by alcohol, and therefore contained no trace of nitrogen.

	Observed vol.	Temp. C.	Difference of mercury level.	Barom^r.	Corrected vol. at 0° C and 1^m pressure.
Gas used (moist)	139·0	8·3°	577·5^{mm}	732·2^{mm}	19·76
After admission of atmospheric air (moist).	487·9	8·3°	213·2 „	731·5 „	241·53
After admission of O (moist).	558·6	8·4°	142·8 „	731·2 „	314·42
After combustion (moist).	502·9	8·3°	199·2 „	731·0 „	255·55
After absorption of CO_2 (dry).	435·8	8·2°	260·5 „	733·1 „	199·95

These numbers lead to the proportion:

$$x : y = 9{\cdot}47 : 10{\cdot}29$$

Or in 100 parts:

Methyl . . .	52·07
Ethyl . . .	47·93
	100·00

It appears, therefore, evident that the easily condensible ethyl is merely mechanically retained in the interstices of the crystals, and gradually evaporates under ordinary atmospheric pressure, but, as the absolute volume of methyl does not perceptibly diminish under the same circumstances, it is highly probable that the latter body enters into the chemical constitution of the crystals.

From the foregoing facts, the decomposition of iodide of ethyl by zinc may be thus expressed:

$$\left.\begin{matrix} C_4\,H_5\,I \\ Zn \end{matrix}\right\} = \begin{matrix} C_4\,H_5 \\ ZnI \end{matrix}$$

A portion of the ethyl thus set free is at the same time decomposed into equal volumes of elayl and methyl:

$$C_4\,H_5 = C_2\,H_2 + C_2\,H_3$$

whilst the iodide of zinc combines with a small proportion of methyl, forming a white crystalline compound, probably of definite constitution. The analyses of the gas *a* indicate a slight excess of methyl over elayl, which would, to a small extent, have been increased had the gases *a* and *β* been collected in the same receiver; this excess of methyl over elayl is without doubt caused by the presence of a trace of moisture either in the iodide of ethyl, or adhering to the zinc, since, as will be shown below, iodide of ethyl and water in contact with zinc are decomposed into oxyiodide of zinc and two volumes of pure methyl.

As ethyl must have a considerably higher boiling point than either elayl or methyl, it might be expected that, on breaking off the extremity of the decomposition tube, the two last named bodies would escape first, and that the gas produced by the ebullition of the last portion of the condensed fluid would be pure ethyl; to ascertain if this were the case, a couple of tubes were charged and subjected to heat, as before described, their capillary extremities were afterwards broken off under quicksilver, and the gas allowed to escape until it issued in a slow regular stream, the beaks of the tubes were then brought beneath a receiver filled with mercury, in which the remainder of the gas was collected. 180 c.c. were obtained from the two tubes. Any elayl or vapour of iodide of ethyl that might be present was absorbed by fuming sulphuric acid, the vapours of which together with sulphurous acid being afterwards removed by a bullet of fused potash.

Two analyses of the gas, made with all the before mentioned precautions, gave the following numbers:

I.

	Observed vol.	Temp. C.	Difference of mercury level.	Barom^{r}.	Corrected vol. at 0° C. and 1^{m} pressure.
Gas used (moist).	90·0	12·6°	626·0^{mm}	751·1^{mm}	9·82
After admission of atmospheric air (moist).	475·9	12·6°	216·4 ,,	751·2 ,,	238·32
After admission of O (moist).	520·7	12·6°	174·9 ,,	751·7 ,,	281·66
After combustion (moist).	484·8	12·5°	208·0 ,,	752·0 ,,	247·17
After absorption of CO_2 (dry).	436·1	11·7°	255·0 ,,	753·3 ,,	208·37
After admission of H (dry).	617·7	12·4°	88·2 ,,	753·2 ,,	392·92
After combustion (moist).	548·2	12·6°	148·4 ,,	752·8 ,,	311·00

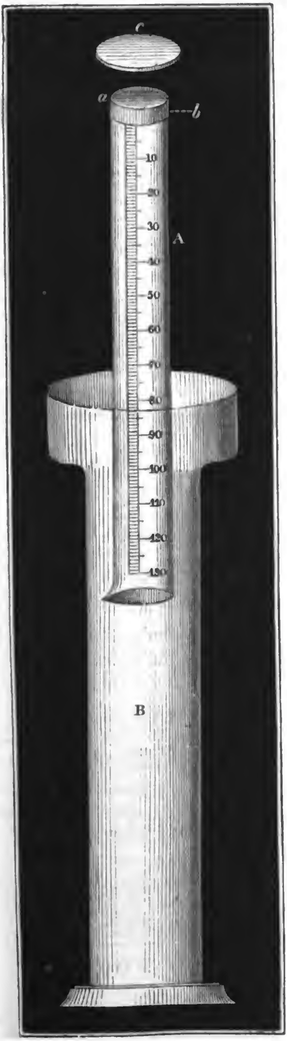
II.

	Observed vol.	Temp. C.	Difference of mercury level.	Barom^{r}.	Corrected vol. at 0° C. and 1^{m} pressure.
Gas used (moist).	91·8	12·8°	623·1^{mm}	752·7^{mm}	10·40
After admission of atmospheric air (moist).	471·2	13·0°	219·9 ,,	752·6 ,,	234·56
After admission of O (moist).	535·1	12·9°	160·6 ,,	751·7 ,,	296·35
After combustion (moist).	498·8	12·8°	194·0 ,,	751·1 ,,	260·19
After absorption of CO_2 (dry).	454·3	13·0°	237·2 ,,	741·5 ,,	218·69
After admission of H (dry).	644·7	13·1°	63·9 ,,	740·8 ,,	416·41
After explosion (moist).	532·7	13·0°	151·8 ,,	740·0 ,,	293·39

These analyses exhibit the following relations between the volumes of combustible gas, oxygen consumed, and carbonic acid generated :

		Vol. of comb. gas.		O. consumed.		CO^2 generated.
I.		9·82		63·47		38·80
	=	1	:	6·46	:	3·95
II.		10·40		67·26		41·50
	=	1	:	6·47	:	3·99

FIG. 3.



The gas consists, therefore, of pure ethyl, which theoretically consumes 6½ times its volume of oxygen, and generates 4 times its volume of carbonic acid, numbers which agree almost exactly with those found in the above analyses.

Although the results just given scarcely admit a doubt as to the identity of the gas with the radical ethyl, yet, in order further to assure myself that the gas was single, and not a mixture, I submitted it to diffusion, which at the same time served to control the previous specific gravity determination. For this purpose a glass tube (*A* Fig. 3) 10 inches long, ¾ inch in diameter, and furnished with an etched millimeter scale, was used; it was stopped at one extremity (*a*) by a plug of gypsum (*b*) 5^{mm} in thickness, the end of the tube being so ground, that whilst it could be closed perfectly gas-tight by the smeared glass plate (*c*), the latter rested very nearly in contact with the surface of the plaister plug. Before use, the instrument was calibrated in the usual manner, the stratum of gypsum perfectly dried, and the upper end of the tube closed by the glass plate: one leg of a small syphon being now inserted into the open extremity of the tube *A*, the latter was immersed with its mouth downwards in the vessel *B*, filled with quicksilver, until the metal came in contact with the inner surface of the plaister plug; the syphon being removed, the tube remained filled with quicksilver, whilst the pores of the gypsum continued open. The gas, perfectly freed from moisture, was now introduced, its volume noted with the proper precautions, and after the tube had been so adjusted, by means of a vertically sliding holder, that the inner and outer quicksilver surfaces stood at the same level, the glass plate was removed, and the diffusion commenced. During the operation, the volume of the gas gradually increased, and therefore to preserve it at the exact pressure of the atmosphere, it was necessary to keep the inner and outer mercury at the same level, by slowly raising the sliding holder. When the diffusion had continued for 10 minutes, it was interrupted by replacing the glass plate in its former position, and the gas, being first dried by a bullet of potash, its volume was again read off.

The mixture of gas, and atmospheric air thus obtained, was divided into two portions, one of which was introduced into a short eudiometer, for the determination of the relative quantities of air and gas present, and the other transferred to a combustion eudiometer, in which it was exploded with atmospheric air and oxygen, the necessary proportions of the two latter being calculated from the composition of the gaseous mixture as indicated by absorption with alcohol in the short eudiometer:

I.

Determination of the augmentation in volume during diffusion.

	Observed vol.	Temp. C.	Difference of mercury level	Barom$^{\mathrm{r}}$.	Corrected vol. at 0° C. and 1$^{\mathrm{m}}$ pressure.
Gas used (dry).	138·2	14·2°	13·4$^{\mathrm{mm}}$	741·9$^{\mathrm{mm}}$	95·70
After diffusion (dry).	158·3	14·1°	3·0 „	741·9 „	111·22

The estimation of the relative quantities of combustible gas and atmsopheric air present in the mixture after diffusion, gave the following numbers:

II.

	Observed vol.	Temp. C.	Difference of mercury level.	Barom$^{\mathrm{r}}$.	Corrected vol. at 0° C. and 1$^{\mathrm{m}}$ pressure.
Gas used (moist).	115·1	14·0°	57·2$^{\mathrm{mm}}$	745·8$^{\mathrm{mm}}$	74·09
After absorption by alcohol.	56·4	14·0°	81·1 „	745·8 „	34·32

The mixture contained, therefore, in 100 parts:

Combustible gas	53·68
Atmospheric air	46·32
	100·0

From these numbers, taken in connection with those given in No. 1, the volume of air which had entered, and the volume of gas that had escaped, during the diffusion, are found to be as follows:

Volume of air entered	51·52
Volume of gas escaped	36·00

The combustion of the second portion of the same mixture, in the large eudiometer, gave the following results:

III.

	Observed vol.	Temp. C.	Difference of mercury level.	Barom^r.	Corrected vol. at 0° C. and 1^m pressure.
Gas used (moist).	134·6	14·2°	583·2^mm	741·3^mm	18·68
After admission of air (moist).	483·7	14·1°	217·9 „	741·6 „	235·35
After admission of O. (moist).	578·5	14·1°	131·2 „	741·6 „	329·17
After combustion (moist).	543·8	13·7°	162·2 „	742·0 „	294·16
After absorption of CO_2 (dry).	495·5	13·6°	207·4 „	744·8 „	253·64

Analyses No. II. and No. III. show that 18·68 vols. of the gaseous mixture contained 10·03 vols. of combustible gas, which consumed 65·50 vols. oxygen, and generated 40·52 vols. carbonic acid, numbers which express the following proportion:

Vol. of comb. gas.		O. consumed.		CO^2 generated.
1	:	6·53	:	4·04

The gas has, therefore, suffered no change in its state of condensation, or in the relative proportion of carbon to hydrogen, by being submitted to diffusion, a result which can only be produced by a single gas, or by a mixture of two or more gaseous bodies, whose relative proportions are expressed by their diffusion coefficients; the latter case must necessarily be of very rare occurrence, and in the present instance can scarcely be admitted as possible. This method might, in almost every case, be employed with advantage, to determine whether or not any specimen of gas be simple or mixed.

The determination of the specific gravity of ethyl, from the above facts, depends upon Graham's well-known law, that the rapidity with which gases diffuse, is directly as their volumes, and inversely as the square roots of their densities; therefore, if we denote the volume of air which entered the diffusion apparatus by (*a*), the volume of gas escaped by (*b*), and the required specific gravity of the gas by (*x*), we have the following equation:

$$a : b = 1 : 1 \frac{1}{\sqrt{x}}$$

from which the following value for x is obtained:

$$x = \frac{a^2}{b^2}$$

If in this equation, we substitute for (*a*) and (*b*) the numbers deduced from analyses II. and III. we obtain:

$$x = \frac{51{\cdot}52^2}{36^2} = 2{\cdot}0481$$

The specific gravity of the mixture of ethyl, methyl, elayl, and nitrogen, was found by weighing, to be 1·525, from which the specific gravity of ethyl is calculated to be 2·0462, a number closely corresponding with that just given.

By employing a long diffusion eudiometer, provided with a mechanical arrangement for regulating the pressure, and by using a perfectly dry porous substance in the place of gypsum, the specific gravities of gases could, no doubt, be determined in this manner with very great accuracy.

The whole of the above facts taken together, prove beyond doubt, when iodide of ethyl is decomposed by zinc, at an elevated temperature, and that the radical ethyl is present amongst the gaseous products, and may easily be separated in a state of perfect purity.

Ethyl is a colourless gas, possessing a very slight ethereal odour,* burning with a brilliant white flame, and having a specific gravity of 2·00394. According to the combined results of the specific gravity and eudiometrical experiments, it contains 2 vols. of carbon vapour and 5 vols. of hydrogen condensed into one volume.

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* This odour, which is at first very strong, probably depends upon the presence of a trace of some foreign body, for after purification by standing over water, and subsequent treatment with fuming sulphuric acid, it almost entirely disappears; perfectly pure ethyl is, therefore, probably, like methyl, inodorous.

2 vols. carbon vapour		= 1·65844
5 vols. hydrogen		0·34550
1 vol. ethyl gas		2·00394
Found	by weighing . .	2·0462
	by diffusion . .	2·0481

It is incondensible at a temperature of — 18° C. (— 0·5° F.).

Allowed to stream slowly through a serpentine glass tube, immersed in a freezing mixture at — 18° C., it retained its gaseous condition unaltered, but at 3° C. (37·5° F.), and exposed to a pressure of $2\frac{1}{4}$ atmospheres, in an Oerstedt's hydrostatic condenser, it is converted into a colourless transparent and mobile liquid, which instantly reassumes the gaseous condition on the pressure being removed; its boiling point, at ordinary pressures, may, therefore, be estimated at about — 23° C. (9·5° F.) 1 vol. of absolute alcohol, at 14·2° C. (58° F.), and 744·8$^{\text{mm}}$ pressure, absorbs about 18·13 vols. of ethyl: agitated with a small quantity of alcohol, over mercury, the gas rapidly disappeared, with the exception of a small bubble, which did not amount to $\frac{1}{10}$ per cent, on afterwards throwing up a few drops of water, the alcohol assumed a milky appearance, followed by a rapid disengagement of gas, which, in a few seconds, amounted to very nearly the original volume. Ethyl is not acted upon by fuming sulphuric acid; it is scarcely affected by concentrated nitric acid and chromic acids, and does not combine with iodine or sulphur, even on the application of heat; in the case of the latter element, sulphuretted hydrogen is copiously evolved, and carbon separated, as the temperature approaches redness. Mixed with half its volume of oxygen, and conducted over spongy platinum, it remains unchanged at ordinary temperatures, but on a gentle heat being applied, the sponge becomes incandescent, water is formed with the simultaneous separation of a small quantity of charcoal, and a gas, probably light carburetted hydrogen, insoluble in alcohol, burning with a feebly illuminating flame, and generating much carbonic acid, is the remaining product of the decomposition. Like methyl, ethyl is not absorbed by perchloride of antimony, even under the influence of bright sunlight; chlorine has no action upon it in the dark, but when equal volumes of the two gases are exposed to diffused daylight, combination rapidly takes place, accompanied by a contraction of volume, and the production of a colourless liquid. Bromine also acts upon ethyl, when exposed to bright sunlight, with the application of a gentle heat. I have not yet completed the examination of the products of this and the former reaction, and must, consequently, defer the communication of further details to a future opportunity.

In the hope of avoiding the formation of methyl and elayl, during the preparation of ethyl, I was led to try what influence the presence of water, alcohol, and ether, would have upon the decomposition of iodide of ethyl by zinc, and although the expectation of preventing the secondary decomposition of the ethyl was not realized, yet the results of the experiments are, in other respects, not wholly uninteresting.

ACTION OF ZINC UPON IODIDE OF ETHYL IN PRESENCE OF WATER.

Equal volumes of water and iodide of ethyl were introduced together with zinc into a decomposition tube, which was then exhausted, hermetically sealed, and exposed to heat, as before described; decomposition commenced and proceeded at a lower temperature than that required for inducing the action of zinc upon iodide of ethyl alone; the fluid contents of the tube became thick and oleagenous, and during the subsequent cooling solidified to a white, soft, amorphous mass. On afterwards opening the tube, under sulphuretted water, a large quantity of gas rushed out with great violence, and was collected in the apparatus, with the precautions already described. No gas was evolved on subsequently treating the residue with water.

The eudiometrical examination of the gas gave the following results:

I.

	Observed vol.	Temp. C.	Difference of mercury level.	Barom^{r}.	Corrected vol. at 0° C. and 1^{m} pressure.
Gas used (dry).	55·9	7·4°	74·9^{mm}	741·3^{mm}	36·27
After action of fuming SO_3 (dry).	55·9	7·7°	73·3 ,,	739·8 ,,	36·24

The gas remaining after the action of fuming sulphuric acid was so nearly absorbed by alcohol, that the extremely small residue could not be estimated.

II.

	Observed vol.	Temp. C.	Difference of mercury vol.	Barom$^{\text{r}}$.	Corr. vol. at 0^0 C. and 1$^{\text{m}}$ pressure.
Gas used (moist).	100·5	8·0^0	621·3$^{\text{mm}}$	739 6$^{\text{mm}}$	10·77
After admission of atmospheric air (moist).	514·1	8·0^0	187·9 „	739·0 „	271·25
After admission of O. (moist).	540·6	8·0^0	162·7 „	738·5 „	298·21
After explosion (moist).	513·9	7·8^0	188·3 „	738·0 „	270·69
After absorption of CO_2 (dry).	488·0	7·6^0	212·0$^{\text{mm}}$	738·1$^{\text{mm}}$	249·78
After admission of H (dry).	717·9	7·7^0	10·2 „	737·9 „	508·08
After explosion (moist).	612·0	8·0^0	100·1 „	737·8 „	374·40

III.

	Observed vol.	Temp. C.	Difference of mercury vol.	Barom$^{\text{r}}$.	Corr. vol. at 0^0 C. and 1$^{\text{m}}$ pressure.
Gas used (moist).	155·0	8·2^0	558·6 „	737·8 „	25·75
After admission of atmospheric air (moist).	521·2	8·0^0	182·1 „	737·3 „	277·08
After admission of O. (moist).	573·0	8·0^0	135·1 „	737·7 „	331·00
After explosion (moist).	509·1	7·8^0	193·1 „	738·0 „	265·79
After absorption of CO_2 (dry).	449·6	7·9^0	246·2 „	738·8 „	215·24
After admission of H (dry).	665·1	8·1^0	52·0 „	737·9 „	443·04
After explosion (moist).	629·2	8·5^0	82·7 „	736·9 „	394·12

These analyses show that the gas does not contain a trace of elayl, and further, that it requires for its combustion 3½ vols. of oxygen generating 2 vols. of carbonic acid:

	Vol. of comb. gas.	O. consumed.	CO_2 generated.
Analysis II.	10·77	37·66	20·91
=	·1	3·50	1·94
Analysis III.	25·75	90·01	50·55
=	·1	3·50	1·97

These are, however, precisely the results obtained in the analysis of methyl* with which this gas exactly coincides in all its properties. It is colourless, nearly insoluble in water, but soluble in alcohol, 1 vol. of which, at 8·8° C. (48° F.) and 665·5^{mm} pressure, absorbs 1·22 volumes; it possesses, at first, a slight ethereal odour, which, by heating the gas first with alcohol, and afterwards with concentrated sulphuric acid, entirely disappears, leaving the methyl perfectly inodorous. It is incondensible at a temperature of —18° C. (—0·5° F.); mixed with chlorine it remains unacted upon in the dark, but in diffused daylight the colour of the chlorine rapidly disappears, proving that combination has taken place; it does not combine with iodine or sulphur even when these substances are heated in the gas.

There can, therefore, be no doubt, that the gaseous product of the decomposition of iodide of ethyl and water by zinc is pure methyl, and that it is identical with the gas evolved by the action of potassium upon cyanide of ethyl,† and by the electrolysis of acetic acid.‡

An attempt to condense methyl, by the application of pressure, was unsuccessful; at 3° C. (37·5° F.) and under a pressure of 20 atmospheres (the highest which the apparatus at my disposal would bear) it exhibited no signs of liquefaction.

The white residue remaining in the decomposition tube, after the escape of the gas, exhaled a strong odour of ether, but contained no other organic substance, the white amorphous mass consisted of oxyiodide of zinc.

The formation of methyl by the action of zinc upon water, and iodide of ethyl is explained by the following equation:

$$C_4\,H_5\,I + HO + 2\,Zn = 2\,(C_2\,H_3) + Zn\,O,\,Zn\,I.$$

The generation of methyl, during this decomposition, might also be explained by assuming, that the radical ethyl is split up into the groups ($C_2\,H_2$) and ($C_2\,H_3$), and that the former is retained in the residue whilst the latter escapes as gas: to convince myself that this was not the case, I submitted a weighed quantity (2·268 grms.) of iodide of ethyl to the action of water and zinc in the manner already described; after the decomposition was ended, and the tube perfectly cooled, the latter was opened, the gas allowed to escape, and the residue quickly mixed with cold oxide of copper and burnt in a combustion tube, as in an ordinary organic analysis. The weight of the potash apparatus increased by 0·132 grms. equivalent to 0·036 grms. carbon: this is, however, only $\frac{1}{5}$ of the quantity of carbon required, if the products of the decomposition are elayl, methyl, and iodide of zinc, for, on this supposition, the residue from 2·268 grms. iodide of ethyl, containing the corresponding quantity of elayl, ought to yield 0·641 grms. carbonic acid (= 0·175 grms. C.) instead of 0·132 grms. as found in the above experiment. The occurrence of a large quantity of oxyiodide of zinc in the residue is also, in itself, a sufficient proof that the ethyl on its separation from iodine is converted, by the assumption of an atom of hydrogen, into 2 vols. of methyl gas.

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* Quarterly Journal of the Chemical Society for April 1848, p. 65.

† Journal of the Chemical Society for April 1848, p. 60.

‡ Annalen der Chemie. Bd., LXIX. s. 279.

This conclusion is also further confirmed by the fact, that iodide of ethyl and water heated in an hermetically sealed tube to the temperature employed in the above production of methyl, are transformed into ether, and a concentrated solution of hydriodic acid. This formation of ether also explains the occurrence of that body in the white residue, and the production of carbonic acid on its subsequent combustion with oxide of copper.

The transformation of iodide of ethyl, in contact with water and zinc, into oxyiodide of zinc and 2 volumes of methyl, furnishes a convenient method for preparing that radical in large quantities perfectly pure; upwards of 300 cubic centimetres being obtained from a single decomposition tube of the dimensions previously stated. It is necessary that the operator should take precautions to preserve himself from the danger attending the possible explosion of the tubes during the decomposition; the apparatus ought, therefore, always to be enclosed in a strong wooden case, open behind, and having a double plate-glass window in front through which the progress of the operation may be watched. The quantity of iodide of ethyl introduced into each tube of the above dimensions, ought not to exceed 3·5 grms., and the temperature of the oil-bath should not be allowed to rise above 180° C. (356° F.) During the whole of the foregoing experiments, no instance of explosion occurred, although the pressure within the tubes must, in many instances, have amounted to between 80 and 100 atmospheres.

ACTION OF ZINC UPON IODIDE OF ETHYL AND ALCOHOL.

This experiment was conducted in precisely the same manner as the last, absolute alcohol being substituted in the place of water.

The appearances presented during decomposition, and the quantity of gas evolved on subsequently opening the tube, were almost exactly identical with those observed in the decomposition of iodide of ethyl in the presence of water. The residue, in which the odour of ether was easily recognized, did not evolve a further quantity of gas on the addition of water.

The eudiometrical analysis led to the following results :

I.

	Observed vol.	Temp. C.	Diff. of mercury level.	Barometer.	Corr. vol. at 0° C. and 1 pressure.
Gas used (dry).	122·7	8·8°	6·1^{mm}	732·3^{mm}	86·32
After action of fuming SO_3 (dry).	120·9	8·2°	8·2 ,,	740·0 ,,	85·89
After removal of specimen for combustion (dry).	84·3	9·0°	43·8 ,,	732·6 ,,	56·21
After absorption by alcohol.	3·1	8·6°	31·9 ,,	732·1 ,,	2·06

II.

	Observed vol.	Temp. C.	Diff. of mercury level.	Barometer.	Corr. vol. at 0° C. and 1^m pressure.
Gas used (moist).	136·7	8·0°	576·9 ,,	741·0 ,,	20·73
After admission of atmospheric air (moist).	504·0	8·3°	192·6 ,,	741·3 ,,	264·37
After admission of O (moist).	574·6	8·4°	128·7 ,,	741·1 ,,	336·81
After explosion (moist).	526·3	8·2°	172·3 ,,	740·9 ,,	286·39
After absorption of CO_2 (dry).	482·3	7·9°	213·2 ,,	738·2 ,,	246·08
After admission of H (dry).	702·0	8·0°	23·7 ,,	737·7 ,,	486·95
After explosion (moist).	566·1	8·1°	140·9 ,,	737·3 ,,	323·44

Analysis No. I, proves the absence of elayl and the presence of 3·66 per cent nitrogen. Analysis No. II, gives the following proportion of combustible gas to oxygen consumed and carbonic acid generated:

	Vol. of comb. gas.		O consumed.		CO_2 generated.
	19·97		70·76		40·31
=	1	:	3·54	:	2·02

The gas has, therefore, the same composition and state of condensation as that evolved by the action of zinc upon iodide of ethyl and water, with which it also exactly coincides in physical properties. The presence of oxyiodide of zinc and ether in the residue leave no room for doubt that 1 eq. iodide of ethyl, with 1 eq. alcohol and 2 eqs. zinc, give rise to 2 eqs. methyl, 1 eq. ether, and 1 eq. oxyiodide of zinc:

$$\left.\begin{array}{r} C_4\,H_5\,I \\ C_4\,H_5\,O.\,HO \\ 2\,Zn \end{array}\right\} \begin{array}{c} 2\,(C_2\,H_3) \\ C_4\,H_5\,O \\ Zn\,O.\,Zn\,I. \end{array}$$

ACTION OF ZINC UPON IODIDE OF ETHYL AND ETHER.

Equal volumes of iodide of ethyl and ether were heated with zinc in a sealed tube, to a temperature of about 150^0 C. (302^0 F.), until the action appeared complete: on being allowed to cool, the residual thick, oily fluid did not solidify. When the beak of the tube was afterwards broken off, only a few cubic inches of gas were evolved, but, on pouring water upon the residue, a strong effervescence, produced by the disengagement of a much larger volume of gas, occurred. The two specimens of gas were collected in the same receiver, and, on being submitted to analysis, yielded the following results:

I.

	Observed vol.	Temp. C.	Diff. of mercury level.	Barometer.	Corr. vol. at 0^0 C. and 1^m pressure.
Gas used (dry).	185·2	12·9^0	19·7^{mm}	744·2^{mm}	128·12
After absorption by SO_3 (dry).	175·1	13·0^0	4·3 „	741·4 „	123·20
After removal of specimen for combustion (dry).	105·7	14·3^0	65·8 „	745·9 „	68·31
After absorption by alcohol.	7·4	14·1^0	71·2 „	746·4 „	4·58

II.

	Observed vol.	Temp. C.	Difference of mercury level.	Barom^r.	Corr. vol. at 0° C. and 1^m pressure.
Gas used (moist).	48·3	13·0°	361·7^{mm}	740·0^{mm}	16·92
After admission of atmospheric air (moist).	312·6	13·1°	92·2 ,,	739·8 ,,	189·83
After admission of O (moist).	355·5	12·7°	48·4 ,,	738·8 ,,	230·82
After combustion (moist).	309·9	12·7°	98·1 ,,	739·4 ,,	186·67
After absorption of CO_2 (dry)	260·5	12·9°	144·6 ,,	738·3 ,,	147·68
After admission of H. (dry)	388·1	13·0°	14·8 ,,	737·9 ,,	267·87
After admission of O (dry).	427·2	13·3°	12·8 ,,	737·3 ,,	295·12
After combustion (moist).	302·0	13·4°	102·4 ,,	737·1 ,,	179·40

According to analysis No. I, the per-centage composition of the gas may be thus expressed :

Gas absorbable by SO_3	3·84
Gas unabsorbable by SO_3	89·71
Nitrogen	6·45
	100·00

Analysis No. II, exhibits the following relation between the volumes of combustible gas, oxygen consumed and carbonic acid generated :

Vol. of comb. gas.		O consumed.		CO_2 generated.
15·83		67·31		38·99
= 1	:	4·25	:	2·46

These numbers indicate that the combustible gas, not absorbed by fuming sulphuric acid, is a mixture, one of the constituents of which must have a higher atomic weight than methyl. From the small residue left after the action of alcohol, which precludes the presence of hydrogen and light carburetted hydrogen, from the occurrence of elayl, and the behaviour of iodide of ethyl in contact with zinc, alone, and in presence of water and alcohol, we may safely conclude that the gas in question is a mixture of ethyl and methyl, and, on applying the formula previously given, we find that the 15·83 vols. of combustible gas, insoluble in fuming sulphuric acid, consist of 4·57 vols. ethyl and 11·26 vols. methyl: therefore, omitting nitrogen, the per-centage composition of the original gas may be thus stated:

Elayl	4·10
Ethyl	27·68
Methyl	68·22
	100·00

Although these experiments cannot by any means be considered as a complete investigation of the action of zinc upon iodide of ethyl in presence of ether, yet they afford sufficient evidence that the separation of the elements of water from the ether has been effected, producing a transformation of ethyl into 2 vols. of methyl; the elements of water have not, however, been so readily eliminated as altogether to prevent the formation of ethyl. The olefiant gas owes its origin, no doubt, to the secondary decomposition of a portion of the ethyl into ($C_2 H_2$) and ($C_2 H_3$), whilst the group ($C_4 H_4$), remaining after the separation of the elements of water from ether, would probably be found in a dark-coloured oily liquid, which collected in small quantity on the surface of the water poured upon the residue in the decomposition tube; the composition of this dark-coloured liquid, and the state in which the gases are retained by the oleagenous residue, have not yet been determined.

In conclusion, I will describe, very briefly, the behaviour of iodide of ethyl in contact with several other metals, at elevated temperatures: after exposure for 12 hours to a heat varying from 150° to 200° C. (302°—392° F.), iron, lead, copper and mercury scarcely affected the decomposition of a trace of iodide of ethyl; but heated with arsenic to about 160° C. (320° F.), the iodide was rapidly decomposed, a heavy blood-red liquid, probably $As I_3$, being formed, which solidifies into brilliant crystals on cooling. The opening of the tube proved that the internal vacuum was unimpaired, and the crystalline mass evolved no gas on being treated with water, in which it was very slightly soluble; the remaining fragments of arsenic possessed a remarkably brilliant metallic lustre, which gave them the appearance of antimony. Tin also effected the decomposition of iodide of ethyl, at about the same temperature; the iodide became gradually replaced by a yellowish oily fluid, which solidified to a crystalline mass on cooling: no gas was evolved either on opening the tube or subsequently treating the residue with water. It would be interesting to ascertain into what combination the radical ethyl enters in the two last decompositions. Finally, iodide of ethyl is rapidly decomposed by potassium, at about 130° C. (266° F.); methyl gas, and a yellowish ethereal fluid which has not been investigated, are the products of the decomposition.

Although the foregoing investigation furnishes the materials, yet I refrain from giving any general views on the probable constitution of the radicals of the series to which ethyl and methyl belong, until I have extended the inquiry to some other members of the same series, as well as to the compounds of the electro-negative class of radicals of which formyl, acetyl, &c. are members.

THE

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CHEMICAL SOCIETY.

November 5, 1849.

The President in the Chair.

The following donations to the Society's Library, since the last Meeting, were announced.

"Report of the Smithsonian Institution," and "Smithsonian Contributions to Science," Vol. I. from the Institution.

"Contributions to the Science of Agriculture," by J. F. W. Johnstone, M.A., from the Author.

"De Saliva," by Nicolaus Jacubowitsch," and "Die Diagnostik verdächtiger Flecke in Criminalfällen," by Carl Schmidt, from Dr. Schmidt.

"On the motion of Gases," Part II., by Thomas Graham, Esq., from the Author.

"Proceedings of the Royal Society of Edinburgh," Nos. 33 and 34, from the Society.

Mr. Henry Sugden Evans, was elected a Fellow of the Society.

The following Papers were read:

XXIX.—*On a new series of Organic Bodies containing Metals and Phosphorus.*

By E. FRANKLAND, Ph. D.

Since submitting to the Society my Memoir on the Action of Zinc upon Iodide of Ethyl, I have been engaged in investigating the action of the same metal upon the corresponding methyl compound; the results, which I shall communicate in a future paper, are nearly analogous, methyl gas is disengaged, and a white crystalline residue remains in the decomposition-tube. The peculiar behaviour of this residue with water, which decomposes it, producing brilliant flame, and causing the evolution of pure light carburetted hydrogen, induced me to study it more closely. When the substance was subjected to distillation in an apparatus filled with dry hydrogen, a colourless pellucid liquid, possessing a peculiarly penetrating and exceedingly nauseous odour, condensed in the receiver; this liquid spontaneously inflames on coming in contact with air or with oxygen, burning with a brilliant greenish-blue flame, and forming dense clouds of oxide of zinc; its vapour, mixed with a large excess of methyl and light carburetted hydrogen, does not inflame spontaneously, but on being ignited, burns with the characteristic flame, depositing upon cold surfaces held within it a black crust of metallic zinc, surrounded by a ring of oxide. This encrustation is easily distinguished from arsenic by its ready solubility in dilute hydrochloric acid with the simultaneous evolution of hydrogen, and by the solution thus obtained affording no reaction with sulphuretted hydrogen. The vapour of this compound is highly poisonous, producing shortly after its incautious inhalation, all the symptoms of poisoning by zinc. It decomposes water with as much violence as potassium, the small tube containing a few drops of the liquid becoming red hot under water; the products of this decomposition are oxide of zinc and two equivalents of pure light carburetted hydrogen, from which it is evident that the body in question is composed of 1 equiv. methyl and 1 equiv. zinc ($C_2\,H_3\,Zn$), for $C_2\,H_3\,Zn + HO = Zn\,O + 2(C\,H_2)$, and this view is confirmed by direct analysis. It is highly probable that this body, which for the present I propose to call *Zincmethyl,* plays the part of a radical, combining directly with oxygen, chlorine, iodine, &c., but my experiments are not yet sufficiently complete to enable me to state this positively.

A corresponding compound, containing ethyl, is also formed during the decomposition of iodide of ethyl by zinc: this body, which may be conveniently named *Zincethyl,* is less volatile, and possesses somewhat weaker affinities than *Zincmethyl;* on decomposition with water it yields oxide of zinc and methyl gas; $C_4\,H_5\,Zn + HO = Zn\,O + 2(C_2\,H_3)$. The existence of this body satisfactorily explains the action of water upon the crystalline compound formed by the decomposition of iodide of ethyl by zinc, as well as the action of these latter bodies upon each other in the presence of water and of alcohol; whilst in the decomposition of ethyl by zinc in presence of ether, there can be little doubt that the zincethyl dissolves in the anhydrous ether without decomposition, and is transformed on the subsequent addition of water into oxide of zinc and 2 vols. of methyl, thus showing that the presence of the latter body in the gaseous products of the decomposition is *not* owing to the decomposition of the elements of water from the ether, as was suggested in my former memoir.

These facts render it highly probable that, in the decomposition of iodide of ethyl by arsenic and by tin, mentioned in the memoir above alluded to, these metals combine with the ethyl, generating compound radicals analogous to cacodyl; in fact, the product of the decomposition by arsenic exhales a most insupportable odour, greatly resembling that which is so characteristic of this radical, whilst a similar decomposition of iodide of methyl would probably yield cacodyl itself. I have also found that the iodides of ethyl, methyl, &c., are readily decomposed by phosphorus, and as no gases are evolved, it is not improbable that a series of bases containing phosphorus analogous to that of Paul Thenard $C_6 H_9 P=(C_2 H_3)\ {}^3P$, may result from this reation.

The existence of hydrogen compounds of arsenic, antimony and tellurium, and the substitution of ethyl and methyl for hydrogen in the new bases of Wurtz, point out the striking similarity between the respective functions of these radicals and of that element, and taken in connection with the above facts, seem to warrant the expectation that most, if not the whole of the following compounds may be obtained. Those marked with an asterisk are already known.

Hydrogen series.	Methyl series.	Ethyl series.	Butyryl series.	Valyl series.	Amyl series.	Phenyl series.
ZnH	$ZnC_2 H_3$*	$ZnC_4 H_5$*	$ZnC_6 H_7$	$ZnC_8 H_9$	$ZnC_{10} H_{11}$	$ZnC_{12} H_5$
$As H_2$	$As (C_2 H_3)_2$*	$As (C_4 H_5)_2$	$As (C_6 H_7)_2$	$As (C_8 H_9)_2$	$As (C_{10} H_{11})_2$	$As (C_{12} H_5)_2$
$Sb H_n$*	$Sb (C_2 H_3)_n$	$Sb (C_4 H_5)_n$	$Sb (C_6 H_7)_n$	$Sb (C_8 H_9)_n$	$Sb (C_{10} H_{11})_n$	$Sb (C_{12} H_5)_n$
$P\ H_3$*	$P\ (C_2 H_3)_3$*	$P\ (C_4 H_5)_3$	$P\ (C_6 H_7)_3$	$P\ (C\ H_9)$	$P\ (C_{10} H_{11})_3$	$P\ (C_{12} H_5)_3$

With a view to obtain these bodies, most of which will probably be found to play the part of radicals, and combine directly with oxygen, chlorine, &c., I have made several preliminary experiments which seem to promise success; these, together with the complete description of the chemical relations of zincmethyl and zincethyl, I will communicate as early as the peculiar difficulties attending their investigation will allow.

Dr. Hofmann exhibited a specimen of the zincmethyl he had obtained from Dr. Frankland, and demonstrated its spontaneous inflammability.

XXX.—*Researches on the Volatile Organic Bases.*

By DR. A. W. HOFMANN.

V. ON THE ACTION OF ACIDS AND BASES UPON CYANILINE.

IN describing the preparation of the salts of cyaniline I had repeated occasion to allude to the rapid decomposition of this base under the influence of acids. I mentioned at that time, that under these circumstances aniline was reproduced, but I had not examined minutely the other products of the same reaction.

To complete the study of cyaniline, it became necessary to investigate carefully the phenomena of this decomposition. My attention was more particularly directed to this subject by the remarkable results, which in the meantime had been obtained in the investigation of other organic cyanogen-compounds, and by the hope of confirming the somewhat unexpected formula which had been elicited in the study of this substance.

Action of Dilute Acids upon Cyaniline.—Cyaniline dissolves with the greatest facility in dilute hydrochloric acid. By concentrated acid the base is at once converted into the hydrochlorate which, like many chlorides, is insoluble in the acid. I have mentioned that the best method for obtaining the hydrochlorate, is to dissolve the base in the dilute acid, and to add immediately fuming acid, when the salt is directly precipitated in the form of white scales; but that I had in vain tried to obtain it by concentrating the dilute solution. The crystals deposited on evaporation, are found to contain scarcely a trace of cyaniline. Some preliminary experiments pointed out at once the complex nature of this crystalline deposit, and a minute investigation proved that it consists of not less than five different compounds, which can be separated only with difficulty.

To obtain these substances separate from each other, a sufficient quantity of cyaniline, half an ounce, was dissolved in dilute hydrochloric acid, and the liquid, which assumed a yellow colour, evaporated on the water-bath. The white crystalline mass thus obtained was washed with cold water, by which a portion was dissolved, which was found to consist entirely of *chloride of ammonium* and *hydrochlorate of aniline.* The solution, possessing in a high degree the remarkable odour which I had repeated occasion to mention in former parts of this inquiry, was carefully tested for oxalic and formic acids, the usual products of the decomposition of cyanogen or hydrocyanic acid, but not a trace of either of these acids could be detected.

The residue, insoluble in cold water, was now repeatedly exhausted with boiling water, by means of which again a separation was effected, leaving a slight crystalline residue, whilst the aqueous solution deposited on cooling crystals which were still a mixture of two compounds, of which the one was much more soluble in water than the other. The compound left after treatment with boiling water was slightly coloured. It appeared desirable to purify it farther, previously to analysis, and as it was found to be soluble in alcohol only with the greatest difficulty, I availed myself of benzole which proved to be a better solvent, although even this liquid took up a very small quantity. On evaporating the benzolic solution, the body separated in shining scales, which became perfectly pure by washing with alcohol. A portion, thus purified, was subjected to combustion with protoxide of copper.

0·3446 grm. of substance gave
0·8795 „ „ carbonic acid, and
0·1565 „ „ water.

Corresponding to the percentage

Carbon . .	69·60
Hydrogen . .	5·04

numbers which represent the composition of *oxanilide*,

$$C_{12} H_6 N, C_2 O_2 = C_{14} H_6 N O_2,$$

as may be seen by the following comparison:

	Theory.		Experiment.
14 equivs. of Carbon	84	70·00	69·66
6 „ „ Hydrogen . .	6	5·00	5·04
1 „ „ Nitrogen . . .	14	11·66	—
2 „ „ Oxygen	16	13·34	—
1 equiv. of Oxanilide . . .	120	100·00	

The deportment of the substance with reagents removed the last doubt respecting its identity with oxanilide; under the influence of a boiling concentrated solution of potash, aniline was evolved, oxalate of potash remaining behind.

The aqueous solution filtered from the impure oxanilide, which, as I mentioned, had deposited a crop of mixed crystals, was evaporated to dryness, together with the crystals, on the water-bath. The separation of this mixture was effected with concentrated alcohol, which left a yellowish residue, and this was found to be insoluble in cold, but slightly soluble in boiling water. Deposited from this solvent after boiling with a small quantity of animal charcoal, it appeared as a snow-white, tasteless, inodorous powder. There was no difficulty in recognizing *oxamide* even by its physical properties, and the ready convertibility of the substance into oxalic acid and ammonia, both by acids and bases, precluded the necessity for a combustion.

It remained to investigate the compound which had been separated from the oxamide by means of boiling alcohol. It was deposited from this solution, partly on cooling, partly after concentration, in snow-white, hair-like flocks, of a satiny lustre. One or two crystallizations from boiling water, in which these flocks were likewise soluble, rendered them pure. This compound was also soluble in ether. It sublimed without decomposition, the sublimate being as light and mobile as precipitated silicic acid.

I have prepared this substance four different times. Each preparation was analysed by combustion.

I. 0·2153 grm. of substance gave :
0·4693 „ „ carbonic acid, and
0·0980 „ „ water.
II. 0·3767 „ „ substance gave :
0·8030 „ „ carbonic acid, and
0·1615 „ „ water.
III. 0·4083 „ „ substance gave :
0·8706 „ „ carbonic acid, and
0·1781 „ „ water.
IV. 0·3811 „ „ substance gave :
0·8124 „ „ carbonic acid, and
0·1676 „ „ water.
V. 0·4573 „ „ substance* gave :
0·5380 „ „ platinum.

Percentage :

	I.	II.	III.	IV.	V.
Carbon . .	59·45	58·13	58·15	58·13	—
Hydrogen .	5·05	4·76	4·84	4·88	—
Nitrogen . .	—	—	—	—	16·71

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* The same preparation as that used in Analysis IV.

This percentage represents the formula:

$$C_8\ H_4\ N\ O_2 \text{ or } C_{16}\ H_8\ N_2\ O_4,$$

which requires the following values:

	Theory.		Mean of Experiments.
16 equivs. of Carbon	96	58·53	58·46
8 „ „ Hydrogen . .	8	4·87	4·88
2 „ „ Nitrogen . .	28	17·07	16·71
4 „ „ Oxygen . . .	32	19·53	—
	164	100·00	

The mean of the analyses agrees much better with theory than the different experiments accord with each other. But this may readily be explained by the long and tedious series of operations which the compound has to undergo previously to analysis. It is obvious that the specimen employed in the first analysis must have still contained a little oxanilide, whilst perhaps some oxamide may have adhered to the latter specimens. The circumstances, however, under which this compound is formed, and the products into which it is decomposed by acids and alkalies, leave no doubt respecting its composition. It is evidently a double compound of *Oxanilide* and *Oxamide,** (Oxanilamide),

$$C_{16}\ H_8\ N_2\ O_4 = C_{12}\ H_6\ N,\ C_2\ O_2;\ \ H_2N,\ C_2\ O_2,$$

corresponding in composition to an analogous compound of carbanilide and carbamide,† which, as I have shown, in my last communication to the Society, is formed in so great a variety of ways.

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* I have tried to obtain some farther confirmation of this formula, by adopting another method of preparing this singular compound. Oxamethane (oxamate of ethyl) yielding, when treated with ammonia, two equivalents of oxamide, it appeared very probable, that by substituting aniline for ammonia the desired compound might be formed according to the following equation:

$$\underbrace{C_4\ H_5\ C_2\ O_4,\ H_2N,\ C_2\ O_2}_{\text{Oxamethane.}} + C_{12}\ H_7\ N = \underbrace{C_4\ H_6\ O_2}_{\text{Alcohol.}} + \underbrace{C_{12}\ H_6\ N,\ C_2\ O_2;\ H_2N,\ C_2\ O}_{\text{Oxanilamide.}}$$

I have not been able to verify this equation by experiment. Aniline appears to act but slowly upon oxamethane: I have not, however, sufficiently varied the experiment; it is possible that by continued action under pressure, by a certain temperature, or in the presence of alcohol and ether, the decomposition may be effected. Incidentally to this experiment, I have tried the action of aniline upon oxalic ether. Oxanilide is formed in this case but likewise only very slowly.

† Carbanilamide having the same composition as urea, in which ammonia is replaced by aniline, and being formed under circumstances analogous to those which give rise to the formation of ordinary urea, I felt inclined, when first (Chem. Soc. Mem. II. 300) I

Carbanilamide . . $C_{12}H_6N, C\ O;\ H_2N, C\ O.$
Oxanilamide . . $C_{12}H_6N, C_2O_2;\ H_2N, C_2O_2.$

Oxanilamide is soluble in a concentrated solution of potassa, with which it cannot, however, remain in contact without decomposition. The solution is perfectly transparent, and acids precipitate unchanged oxanilamide; after a short period, however, varying with the concentration of the solution and the temperature, the liquid becomes turbid in consequence of the separation of droplets of aniline, whilst an evolution of ammonia at the same time becomes perceptible. The solution now contains a large quantity of oxalic acid. The following equation explains this decomposition:

$$\underbrace{C_{16}H_8N_2O_4}_{\text{Oxanilamide.}}+2(HO, KO)=2\,KC_2O_4+\underbrace{C_{12}H_7N}_{\text{Aniline.}}+H_3N.$$

Dilute sulphuric acid has no effect upon oxanilamide. Concentrated acid evolves equal volumes of carbonic acid and carbonic oxide, sulphanilic acid and sulphate of ammonia remaining behind:

$$\underbrace{C_{16}H_8N_2O_4}_{\text{Oxanilamide.}}+3HSO_4=2CO_2+2CO+\underbrace{C_{12}H_7NS_2O_6}_{\text{Sulphanilic acid.}}+H_4N\,SO_4.$$

The products of the action of hydrochloric acid upon cyaniline accordingly are:

Chloride of ammonium,
Hydrochlorate of aniline,
Oxanilide,
Oxamide, and
Oxamide-oxanilide.

The formation of these substances is intelligible at the first glance; it is due to the propensity which even in its conjugated state

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found this compound, to consider it as the urea of aniline; subsequent researches, however, (Chem. Soc. Qu. J. II. 35) showing that this compound has no basic properties whatever, induced me to abandon this view, and to consider the so-called anilo-urea as a double compound of carbamide and carbanilide. Since that period, the true anilo-urea, possessing all the properties which we are justified in expecting in such a compound, has been discovered by M. Chancel (Compt. Rend. XXVIII. 293), who found that nitrobenzamide, discovered by Mr. Field (Chem. Soc. Mem. III. 404) when subjected to the action of hydrosulphuric acid, is converted into *anthranilamide* or *anilo-urea*. This compound is basic like ordinary urea; it is isomeric with the substance described by me under the name of carbanilamide (carbamide-carbanilide) and produced especially by the action of cyanic acid upon aniline, or by the double decomposition of aniline-salts with metallic cyanates.—With regard to carbanilide, a substance of the same composition (?) has been of late obtained by MM. Chancel and Laurent (Instit. 1848, 95). This compound, *flavine*, which is formed by the action of hydrosulphuric acid upon dinitrobenzophenone, is basic; it is only isomeric not identical with carbanilide.

cyanogen retains, to assimilate the elements of water; one equivalent of cyaniline and two equivalents of water contain the elements of one equivalent of ammonia and one equivalent of oxanilide:

$$\underbrace{C_{14}\,H_7\,N_2}_{\text{Cyaniline.}}+2HO+HCl=\underbrace{C_{12}\,H_6\,N,\,C_2\,O_2}_{\text{Oxanilide.}}+H_4\,N\,Cl,$$

and they likewise represent one equivalent of oxamide and one equivalent of aniline:

$$\underbrace{C_{14}\,H_7\,N_2}_{\text{Cyaniline.}}+2HO+HCl=\underbrace{H_2\,N,\,C_2\,O_2}_{\text{Oxamide.}}+\underbrace{C_{12}\,H_7\,N,\,HCl.}_{\text{Hydrochlorate of Aniline.}}$$

The formation of oxanilamide requires no farther elucidation, this substance being a double compound of the two preceding bodies.

The simultaneous production of oxamide, oxanilide, and the double compound, suggested the idea that the latter might be the principal product of the reaction, whilst the two former would appear as resulting from a farther decomposition of the latter. This, however, does not appear to be the case. Often as I repeated this experiment, I invariably obtained the three compounds in nearly equal proportions, nor did I succeed in splitting oxanilamide into its proximate constituents by the action of dilute acids or alkalies, or by continuous ebullition. The application of heat likewise, which in the case of carbanilamide had led to such decided results, was unsuccessful, oxanilamide, as mentioned before, being volatile without decomposition.

The action of dilute sulphuric acid on cyaniline gives rise to perfectly similar phenomena.

The deportment of cyaniline with dilute acids offers an unequivocal proof of the correctness of the formula, which I have proposed for this compound. Only in direct combination with aniline is cyanogen capable of yielding oxanilide and oxamide; had it been present in the state of hydrocyanic acid, as e. g. in hydrocyanoharmaline, formanilide and formamide would have been the products of decomposition; lastly, if cyaniline had been produced in consequence of a substitution-process, we should have expected the formation of cyanic acid, and a corresponding compound in the aniline-series, or their products of decomposition, carbonic acid, &c.

Action of Concentrated Sulphuric Acid on Cyaniline.—Not less characteristic of the constitution of cyaniline is the deportment of this substance with concentrated sulphuric acid. It dissolves in this acid with a violet colour; the solution, when slightly heated, evolves equal volumes of carbonic acid and carbonic oxide; on strongly heating, the proportion of carbonic oxide decreases, sulphurous acid being disengaged; after cooling, the liquid solidifies into a crystalline mass of sulphanilic acid, sulphate of ammonia being formed at the same time:

$$\underbrace{C_{14}\,H_7\,N_2}_{\text{Cyaniline.}} + 2H\,SO_4 + 2HO = \underbrace{C_{12}\,H_7\,N\,S_2\,O_6}_{\text{Sulphanilic acid.}} + H_4N\,SO_4 + CO_2 + CO.$$

The decomposition illustrated by the preceding equation, is in perfect accordance with the assumption of a direct combination of aniline with cyanogen; if hydrocyanic acid had been present, carbonic oxide only could have been evolved, while in the case of cyaniline being a substitution-product, the action of sulphuric acid should have given rise to the disengagement of carbonic acid only.

Action of Bromine upon Cyaniline.—I have made a few experiments on the deportment of cyaniline with bromine, the results of which are perfectly intelligible after the preceding remarks respecting its behaviour with acids.

Cyaniline is violently attacked by bromine; the first product of the action appears to be a substitution-body, most probably tribromocyaniline; under the influence, however, of the free hydrobromic acid, formed in the reaction, and assisted by the simultaneous evolution of heat, the greater part of the cyanogen-base undergoes the changes which I have detailed in the preceding pages; and the aniline separates in the form of tribromaniline which, if alcohol has been present in the reaction, crystallizes in beautiful needles, as soon as the solution has become cool. The bromine-body was identified by analysis.

0·4000 grm. of substance gave
0·3315 „ „ carbonic acid, and
0·0575 „ „ water.

	Experimental percentage of	Theoretical percentage in tribromaniline.
Carbon . . .	22·60	22·50
Hydrogen . . .	1·59	1·25

Action of Alkalies upon Cyaniline.—This substance is only very slowly and difficultly attacked by potash or soda. Cyaniline may be boiled with either an aqueous or alcoholic solution of potash for hours, without undergoing the slightest change. Only when fused with solid potash does decomposition take place, aniline, together with ammonia, being evolved. I naturally expected that the residue should contain oxalate of potash; but in repeated experiments not a trace of this salt was observed. The action on cyaniline takes place only at a temperature at which the oxalic acid is converted into carbonic acid with evolution of hydrogen; in an apparatus appropriately arranged, the hydrogen evolved in the decomposition of cyaniline by potash may be easily collected. Hence the reaction ensues according to the following equation:

$$\underbrace{C_{14}\,H_7\,N_2}_{\text{Cyaniline.}} + 2\,(HO, KO) + 2HO = \underbrace{C_{12}\,H_7\,N}_{\text{Aniline.}} + H_3N + H + 2\,(KO, CO_2)$$

VI. METAMORPHOSES OF DICYANOMELANILINE.

FORMATION OF THE ANILINE-TERM CORRESPONDING TO CYANIC ACID.

In describing the bases, which are derived from melaniline, I have mentioned a compound which is formed by the action of cyanogen-gas upon an alcoholic solution of melaniline, and to which I have given the name dicyanomelaniline.* This substance bears in its constitution the greatest resemblance to cyaniline; in its formation melaniline and cyanogen have combined without elimination of hydrogen, but while, in producing cyaniline, the original aniline-atom assimilated but one equivalent of cyanogen, the complex structure of melaniline, which arises from the combination of two aniline-atoms, was exhibited even in its deportment towards cyanogen-gas, two equivalents of which are fixed in this reaction, the analysis having led to the formula:

$$C_{30}\,H_{13}\,N_5 = Cy_2\,C_{26}\,H_{13}\,N_3.$$

In the paper on melaniline, I have noticed the remarkable instability of dicyanomelaniline; I have mentioned that the action of reagents and especially of acids, on this substance, gives rise to a great variety of phenomena of decomposition, a more minute investigation of which, however, was deferred until the study of the corresponding metamorphoses of cyaniline was completed.

The following pages are devoted to a more detailed account of these phenomena.

In dicyanomelaniline the basic properties of the melaniline-atom are still perceptible, but in a degree very inferior to that observed in the compounds arising from melaniline by substitution. I have vainly endeavoured to produce crystallized combinations of dicyanomelaniline with acids, although such bodies are readily formed with the substitution-bases; in fact the only experimental evidence of the basic nature of this substance, is the remarkable facility with which

* Chem. Soc. Qu. J. i. 285.

it dissolves in mineral, as well as vegetal acids, from which solutions it is re-precipitated by the addition of potash or ammonia. The re-precipitation of unaltered dicyanomelaniline, however, can only be ensured, if the solution in acids be saturated immediately with the alkali; after a short time, varying with the strength and concentration of the acid employed, decomposition sets in, and the liquid soon ceases to contain a trace of the cyanogen-base.

When speaking of cyaniline, I have mentioned that the solutions of salts of this base can exist only for a limited period; the transformation of the corresponding melaniline-compound goes on with much greater rapidity, and whilst in the former case, the decomposition proceeds only gradually, the change in the latter substance is effected almost instantaneously.

Dicyanomelaniline dissolves in hydrochloric acid of ordinary concentration, to a clear, slightly yellow liquid, which if immediately saturated with ammonia, yields a precipitate, consisting of the cyanogen-compound with all its original properties; if on the contrary, the solution be allowed to stand for a minute or two, it suddenly becomes turbid, and deposits a slightly yellowish mass, presenting an indefinite crystalline appearance. This change takes place almost simultaneously with solution, if very concentrated hydrochloric acid be employed, or if the dilute solution be gently heated. The mother-liquor from which the new compound has been deposited, contains a very considerable proportion of chloride of ammonium.

The yellowish substance is but slightly soluble in water, by means of which it may be easily purified from hydrochloric acid. It dissolves somewhat difficultly in boiling alcohol, from which it is slowly deposited in a crystalline crust, presenting a more individual appearance than the original precipitate. The disinclination of this compound to assume a very definite crystalline form,—frequently it separates as a resinous mass, assuming only very slowly crystalline structure—renders it difficult to obtain it in a state of perfect purity. In the following analyses, specimens of different preparations, dried at 100° C. were employed. Analysis V. refers to a substance obtained by re-crystallizing the compound used in analysis IV.

I. 0·3277 grm. of substance gave:
0·8100 „ „ carbonic acid, and
0·1195 „ „ water.
II. 0·3160 „ „ substance gave:
0·7810 „ „ carbonic acid, and
0·1200 „ „ water.

III. 0·2805 „ „ substance gave:
0·6969 „ „ carbonic acid, and
0·1041 „ „ water.
IV. 0·4175 „ „ substance gave:
0·4527 „ „ platinum.
V. 0·5065 „ „ substance gave:
0·5657 „ „ platinum.

Percentage-composition:

	I.	II.	III.	IV.	V.
Carbon . .	67·41	67·40	67·76	—	—
Hydrogen .	4·05	4·21	4·12	—	—
Nitrogen . .	—	—	—	15·38	15·84

These numbers may be translated into the expression:

$$C_{30}H_{11}N_3O_4,$$

as is evident from the following comparison of the theoretical with the experimental values.

	Theory.		Mean of experiments.
30 equivs. of Carbon . .	180	67·92	67·52
11 „ „ Hydrogen .	11	4·15	4·12
3 „ „ Nitrogen .	42	15·84	15·40
4 „ „ Oxygen . .	32	12·09	—
	265	100·00	

This formula readily explains the transformation of dicyanomelaniline under the influence of acids. One equivalent of this substance assimilates four equivalents of water, while two equivalents of ammonia combine with the acid.

$$\underbrace{C_{30}H_{13}N_5}_{\text{Dicyanomela-niline.}} + 4HO + 2HCl = \underbrace{C_{30}H_{11}N_3O_4}_{\text{Yellowish compound.}} + 2H_4NCl.$$

A simple method of controlling this equation, presented itself in the determination of the amount of nitrogen, eliminated in the form of ammonia from a given quantity of dicyanomelaniline, when treated with hydrochloric acid. In performing this experiment

2·2529 grm. of dicyanomelaniline gave:
3·9415 „ „ bichloride of platinum and ammonium.

Accordingly 100 parts of the cyanogen-body, yielded 10·97 parts of nitrogen, the amount deduced from the above equation is 10·65.

This determination leaves no doubt respecting the composition of the new substance, and this is moreover supported by various phenomena of transformation which I shall describe hereafter. The formula derived from analysis, although correctly enumerating the elements grouped in the yellow compound, leaves us quite in the dark respecting their actual arrangement, and consequently of the position which has to be assigned to the substance. A rational interpretation of the analysis, was, however, greatly facilitated by the previous study of the decomposition of cyaniline. The conversion of this substance into oxalates of aniline and ammonia, or rather into compounds derived from those salts by elimination of water, (oxanilide and oxamide), at once gave the clue to the nature of the yellow crystals. They may be considered as binoxalate of melaniline, less 4 equivs. of water.

$$C_{26}\,H_{13}\,N_3,\ H\,C_2\,O_4 + H\,C_2\,O_4 = C_{30}\,H_{15}\,N_3\,O_8$$
$$\underbrace{C_{30}\,H_{15}\,N_3\,O_8}_{\text{Binoxalate of Melaniline.}} - 4\,HO = \underbrace{C_{30}\,H_{11}\,N_3\,O_4}_{\text{Yellow compound.}}.$$

Experiment supports this view in an unequivocal manner. On adding ammonia or potash to an alcoholic solution of the compound, the liquid readily solidifies into a crystalline mass; these crystals are pure melaniline; the mother liquor contains a considerable proportion of oxalic acid. To avoid any possible mistake, I have identified the melaniline produced in this reaction, by preparing the platinum-salt and determining the platinum.

0·3482 grm. of platinum-salt gave:
0·0825 „ „ platinum.

Percentage of platinum.	Percentage of platinum from melaniline-salt.
23.69	23·65

The substance then to which the action of acids upon dicyanomelaniline gives rise, belongs to a daily increasing class of bodies which are derived from acid salts of ammonia, or of organic bases, by elimination of 4 equivs. of water. Succinimide, (D'Arcets' bisuccinamide) and camphorimide, (bisuccinate and bicamphorate of oxide of ammonium—4 equivs. of water), were some of the first members of this class, with which we became acquainted, and in which at a certain period, the pre-existence of imidogen (HN) was assumed. In the aniline-series, likewise, several representatives of this group have been obtained by Laurent and Gerhardt, who have proposed the term *aniles* for these compounds, succinanile, camphoranile, phtalanile designating, in the aniline-series, the terms corresponding to succinimide, camphorimide, and phtalimide. Hence the term *melanoximide,* or *oxamelanile,* might be applied to the new compound. It is worthy of remark, that the oxalic acid member corresponding to melanoximide is known, neither in the ammonia-, nor in the aniline-series.

Substances produced by dehydration, such as oxamide, oxamic acid, succinimide, &c., are reconverted into the compounds from which they are derived, not only by the action of alkalies, but likewise by the influence of acids. I was, therefore, desirous to ascertain, whether binoxalate of melaniline might be reproduced from melanoximide by treating it with acids. This substance being nearly insoluble in dilute acids, sulphuric or hydrochloric, their action is but extremely slow; an alcoholic solution of melanoximide, however, is rapidly affected by acids, especially at the temperature of ebullition. On boiling a solution of this body in strong hydrochloric acid, it assumes a deep yellow colour, the peculiar somewhat cyanic odour, which I had frequent opportunities of noticing during these investigations, being evolved in a remarkable manner. After a few minutes the solution again becomes colourless, when the presence both of oxalic acid, and of melaniline* in the liquid, may be traced without difficulty, showing that under the influence of acids also, the 4 equivs. of water are re-assimilated. Oxalic acid and melaniline are, however, by no means the only products of this reaction, for on cooling, the solution deposits long beautiful needles, containing neither melaniline nor oxalic acid, the examination of which is not yet finished; the solution contains, moreover, a perceptible quantity of ammonia.

Several of the imidogen-compounds which have been examined, such as camphorimide, and phtalimide, have the properties of weak acids, they combine, for example, with protoxide of silver. The actual nature of these combinations is scarcely understood. Some consider them as compounds of the imides with the oxides, others as imides in which hydrogen is replaced by silver; melanoximide is likewise feebly acid, it dissolves in very weak solutions of ammonia and potash without decomposition, and may be obtained again from these solutions, with all its properties, on the addition of an acid. Prolonged contact, however, with alkalies, especially when concentrated, as stated before, gives rise to assimilation of water, binoxalate of melaniline being formed. A solution of melanoximide in dilute alcohol, especially when containing a few drops of ammonia, yields a slightly yellowish amorphous precipitate with nitrate of silver. The analysis of this silver-compound has not led to any precise result: by igniting three different specimens of the silver-salt, a percentage greatly varying (25·41—28·57, and 30·5 of silver) was obtained. A compound of melanoximide with 1 equiv. of protoxide of silver, would contain 28·4 per cent of silver. To the acceptation, however, of such a compound, farther experimental evidence would be requisite.

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* The reproduction of melaniline from melanoximide by the action of acids, was likewise proved by the preparation and analysis of a platinum-salt; 0·3177 grm. of salt gave 0·1206 grm. = 23·29 per cent of platinum. The theoretical percentage of platinum in the melaniline-salt is 23·65.

It remained now only to try whether melanoximide, the nature of which appeared to be sufficiently established by the preceding experiments, might not be actually obtained by the action of heat, either alone, or assisted by agents of dehydration, upon binoxalate of melaniline, a salt which I have mentioned in the description of melaniline.* Here a difficulty presented itself at once in the facility with which melaniline is decomposed when heated: it appeared by no means easy to regulate the temperature in such a manner, as to confine the reaction to an elimination of water, without affecting the residuary compound. Nor have I—it may at once be stated—been able to effect the desired conversion; the experiment, however, although unsuccessful as to its intended object, has led to a result as remarkable as any that has been elicited in the course of these researches.—On heating binoxalate of melaniline, the salt fused and entered soon into a sort of ebullition, torrents of carbonic oxide, and carbonic acid, being evolved; towards the end of the operation a splendid crystalline sublimate appeared in the neck of the retort, which was found to be carbanilide, while a transparent viscid mass, solidifying on cooling into a resin-like substance, remained behind. The gas which is evolved in this process, possessed in a very powerful degree, the peculiar odour to which in this, as well as in former communications, I have repeatedly alluded. Never, indeed, had I met before with a reaction, which appeared to give rise to so large a quantity of this peculiar compound, and I began to hope that I should at last succeed in securing this enigmatical body, which I had vainly chased on so many occasions. My endeavours, however, to condense this substance from the mixture of carbonic oxide and carbonic acid, in which it was diffused, were fruitless; and I did not succeed until I began to study the action of heat on melanoximide itself, instead of on binoxalate of melaniline.

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* Chem. Soc. Qu. J. I. 285.

Action of Heat on Melanoximide. Anilocyanic Acid, (Carbanile.)— The dry distillation of melanoximide presents phenomena similar to those observed on heating binoxalate of melaniline. The mass fuses and evolves a large quantity of gas, in which, however, the presence of carbonic oxide predominates to such an extent, that in certain stages of the process scarcely any carbonic acid is detected. During the disengagement of the gas, a slightly yellow liquid distils over, of a most powerful odour, recalling at once the odour of aniline, of cyanogen, and hydrocyanic acid, provoking lachrymation in a most fearful manner, and exciting too in the throat, the suffocating sensation produced by the latter. Small quantities of this liquid, which is by no means very volatile, evaporate in the gas which is evolved during the process, and impart to it this penetrating odour in such a degree, that it is necessary to collect the gas, in order to escape its irritating action on the nose and eyes. Towards the end of the distillation, on raising the temperature very considerably, together with the liquid, a solid body is evolved, which is deposited in radiated crystals on the neck of the retort, and carried over into the receiver, while a slightly coloured, transparent, resin-like compound remains in the retort, very similar to the residue obtained in the dry distillation of melaniline. The quantity of crude liquid obtained in this process, amounts to about ten per cent of the melanoximide employed; it is necessary to avoid as carefully as possible, the presence of moisture either in the substance to be distilled, or in the retort or receiver, in order not to reduce still farther in quantity the product of the operation, the liquid being readily decomposed by water. This deportment explains, why in the distillation of binoxalate of melaniline (distinguished from melanoximide only by containing 4 equivs. of water more), only traces of this liquid are obtained. It is evident that the elimination of water, and the formation of the compound take place simultaneously, decomposing each other at the very moment of their liberation.*

In purifying the yellow liquid, the white crystalline matter with which it is always contaminated, has to be separated. This cannot be effected by distillation, the boiling-points of the two bodies being so very close to each other, that the distillate invariably contains again a portion of the crystals. The separation succeeds best by cooling the liquid, in order to cause as complete a deposition of the crystalline matter as possible, and filtering through fine bibulous paper. A very limited quantity of the compound being at my disposal, I contrived to filter it as perfectly as possible by atmospheric pressure, the funnel being fixed by means of a perforated cork into a little flask, from which part of the air had been expelled by heat. On cooling, the liquid was forced through the paper, while the crystalline compound remained on the filter. The presence of moisture having been carefully excluded in all the operations, it was now sufficient to rectify the liquid, in order to obtain it in a state fit for analysis; on distillation in a glass tube, the liquid entered into regular ebullition at 178° C.; during the latter part of the distillation, the thermometer rose very gradually to 180° C. Thus obtained, the substance formed a colourless, very mobile liquid, heavier than water, strongly refracting light, and possessing the powerful odour in undiminished intensity.

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* I have endeavoured to avoid the liberation of the water, by mixing the binoxalate with anhydrous phosphoric acid. The result, however, was not satisfactory, nearly the whole mass being charred.

For the following analyses, specimens of different preparations were employed. Carbon-determination I. was made with a product of a first operation, prepared at a period at which I was less acquainted with the habits of the substance in question; carbon-determination II. and nitrogen-determination III. refer to a specimen prepared at a later period, and on a larger scale. When burnt with protoxide of copper:

I. 0·2041 grm. of liquid gave:
0·5226 ,, ,, carbonic acid, and
0·0810 ,, ,, water.
II. 0·2610 ,, ,, liquid gave:
0·6720 ,, ,, carbonic acid, and
0·1020 ,, ,, water.

The nitrogen was estimated, by passing the vapour of the liquid over a long layer of soda-lime, and proceeding with the resulting mixture of ammonium- and aniline-platinum-salts, as indicated in the analysis of cyaniline.*

III. 0·4557 grm. of liquid gave:
0·3830 ,, ,, platinum.

Percentage-composition:

	I.	II.	III.
Carbon . . .	69·83	70·21	—
Hydrogen . .	4·40	4·34	—
Nitrogen . .	—	—	11·92

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* Chem. Soc. Qu. J. I. 159.

These numbers, especially if we rely more particularly on the results obtained in the analysis of the second specimen, may be expressed by the formula:

$$C_{14}\,H_5\,N\,O_2,$$

which requires the following values:

14 equivs. of Carbon . . .	84	70·58
5 „ „ Hydrogen . .	5	4·20
1 „ „ Nitrogen . .	14	11·76
2 „ „ Oxygen . .	16	13·46
1 equiv. of the odorous Compound .	119	100·00

The preceding formula is corroborated by a series of reactions of remarkable precision, presenting perhaps, when taken as a whole, a higher order of experimental evidence than can be obtained from any elementary analysis, however accurate it might be.

Before entering into a detailed account of these reactions, the position of the new compound may be directly fixed by the inquiry, whether a corresponding term exists in the ammonia-series. By subtracting from the above formula the elementary difference, distinguishing aniline from ammonia, namely $C_{12}\,H_4$, we arrive at once at a well-known formula:

$$\begin{aligned} C_{12}\,H_7\,N \quad &- C_{12}\,H_4 = \quad H_3\,N. \\ C_{14}\,H_5\,N\,O_2 &- C_{12}\,H_4 = C_2\,H\,N\,O_2. \end{aligned}$$

The formula $C_2\,H\,N\,O_2$ expresses the composition of hydrated cyanic acid, and accordingly the new compound would represent in the aniline-series the term cyanic acid; or in other words the odorous liquid would stand in the same relation to aniline, as hydrated cyanic acid stands to ammonia.

The reactions of cyanic acid being very clearly defined, there was no difficulty in tracing, by experiment, the analogy of the two compounds. It may here at once be stated, that this analogy has been found to be perfect in almost every direction, so that for the sake of shortness, I will designate the liquid in question, by the name *anilo-cyanic acid,* although, from reasons which will soon be evident, I have not been able to produce compounds analogous to the cyanates.

The action of acids and bases upon anilo-cyanic acid, appeared to offer the first standard of comparison. Both classes of agents convert cyanic acid into ammonia, and carbonic acid, 2 equivs. of water being assimilated. Exactly the same effect is exerted on anilo-cyanic acid. This compound is readily attacked by potash, or hydrochloric acid, aniline, or carbonic acid being evolved, while carbonate of potash, or hydrochlorate of aniline remains behind:

$$\begin{aligned} C_2\,H\,N\,O_2 + 2\,HO &= H_3\,N + 2\,CO_2. \\ C_{14}\,H_5\,N\,O_2 + 2\,HO &= C_{12}\,H_7\,N + 2\,CO_2. \end{aligned}$$

If concentrated sulphuric acid be employed instead of hydrochloric we obtain in the place of hydrochlorate of aniline, sulphanilic acid, as might have been expected.—Cyanic acid is capable of fixing water, even if acids and alkalies be absent, in this case, however, the metamorphosis extends over two equivalents. The ammonia eliminated in the decomposition of the first, combines with a second equivalent of cyanic acid not yet affected, urea or bicarbamide being produced with evolution of carbonic acid. In a similar manner anilo-cyanic acid, when treated with water, gives off carbonic acid very slowly at common temperatures, more rapidly however on the application of heat, while the oil is converted into a crystalline mass.

The crystals thus formed are insoluble in water but dissolve in alcohol; they have all the properties of carbanilide.* The following combustion would have been scarcely necessary.

0·1743 grm. of crystals gave
0·4675 „ „ carbonic acid, and
0·9040 „ „ water.

Percentage:

	Experimental.	Theoretical, in carbanilide.
Carbon . . .	73·15	73·58
Hydrogen . .	5·76	5·66

If we recollect that urea may be viewed as bicarbamide, the analogy of the reactions of both cyanic acids with water becomes at once perceptible, the one yielding 2 equivs. of carbamide, the other 2 equivs. of carbanilide, as exhibited by the following equations:

$$\begin{aligned} 2\,C_2\,H\,N\,O_2 + 2\,HO &= C_2\,H_4\,N_2\,O_2 + 2\,CO_2 \\ C_2\,H_4\,N_2\,O_2 &= 2\,(H_2\,N, CO) \\ 2\,C_{14}\,H_5\,N\,O_2 + 2\,HO &= C_{26}\,H_{12}\,N_2\,O_2 + 2\,CO_2 \\ C_{26}\,H_{12}\,N_2\,O_2 &= 2\,(C_{12}\,H_6\,N, CO). \end{aligned}$$

Not less symmetrical are the changes which the two analogues undergo when treated either with aniline or with ammonia. Cyanic acid when treated with aniline yields carbamide-carbanilide; anilo-cyanic acid on the other hand yields carbanilide.

$$\begin{aligned} C_2\,H\,N\,O_2 + C_{12}\,H_7\,N = C_{14}\,H_8\,N\,O_2 &= H_2\,N, CO + C_{12}\,H_6\,N, CO \\ C_{14}\,H_5\,N\,O_2 + C_{12}\,H_7\,N = C_{26}\,H_{12}\,N\,O_2 &= C_{12}\,H_6\,N, CO + C_{12}\,H_6\,N, CO. \end{aligned}$$

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* Chem. Soc. Qu. J. II. 36.

In the same manner anilo-cyanic acid, when heated with ammonia is converted into carbamide-carbanilide, whilst the action of ammonia on cyanic acid itself gives rise to the production of urea or bicarbamide.

$$C_2\,H\,N\,O_2 + H_3\,N = C_2\,H_4\,N_2\,O_2 = H_2\,N, C\,O + H_2\,N\,CO,$$
$$C_{14}\,H_5\,N\,O_2 + H_3\,N = C_{14}\,H_8\,N_2\,O_2 = H_2\,N, C\,O + C_{12}\,H_6\,N, CO.$$

These several reactions are effected instantaneously on adding either ammonia or aniline to the oil, which at once solidifies, a considerable amount of heat being disengaged. It is not unlikely that a similar effect may be produced by all ammonides, (a term which may be used for the class of bases represented by ammonia); a small quantity of cumidine having remained in the collection of the College from Mr. Nicholson's investigation I placed the two substances in contact; the mixture solidified at once to a crystalline mass; the product not being in sufficient quantity for combustion was not examined farther; there cannot, however, remain the slightest doubt that it is a double compound of carbanilide and carbocumidide, analogous to carbamide-carbanilide, and oxamide-oxanilide, whose formation may be represented by the following equation:

$$C_{14}\,H_5\,N\,O_2 + C_{18}\,H_{13}\,N = C_{32}\,H_{18}\,N_2\,O_2 = \begin{cases} C_{12}\,H_6\;\,N, CO, \\ C_{18}\,H_{12}\,N, CO. \end{cases}$$

Toluidine and even leucoline, which is remarkable for its disinclination to form crystalline derivatives, exhibit a similar deportment.

Anilo-cyanic acid, when acting upon the various alcohols, on pyroxylic spirit, wine-alcohol, and fusel-oil, and even on hydrated oxide of phenyl (carbolic acid) gives results not less marked; and here again an analogy with ordinary cyanic acid may be traced to a very great extent.

Anilo-cyanic acid dissolves in the alcohols with considerable evolution of heat, clear liquids being formed, which after some minutes deposit magnificent crystals. These crystals are readily fusible at the boiling temperature of water, they are insoluble in this liquid, but soluble in all proportions in alcohol and ether.

The bodies to which these reactions give rise are generally mixtures; and it is but with difficulty that the individual components are separated. I cannot at this moment offer to the Society definite numbers unequivocally fixing the composition of these bodies; however from approximative combustions,* performed with substances not absolutely pure, and employed in quantities insufficient to secure an accurate determination of the hydrogen, I have already formed a decided opinion respecting the nature of the substances produced in these reactions.

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* Not knowing whether and when I shall be allowed to return to this investigation, I here subjoin the numbers obtained in the combustion both of the methyl- and ethyl-

From the researches of Liebig and Wöhler on the action of cyanic acid upon the alcohols, we know that the latter class of bodies is capable of directly fixing either one or two equivalents of the former. Two classes of compounds are thus produced, the urethanes or carbamic ethers (obtainable also in a variety of other remarkable reactions), and the substances termed allophanic ethers.

$$\underbrace{C_4\,H_6\,O_2}_{\text{Alcohol.}} + \underbrace{H\,C_2\,N\,O_2}_{\text{Cyanic acid.}} = \underbrace{C_6\,H_7\,N\,O_4}_{\substack{\text{Urethane}\\ \text{Carbamate of ethyl.}}}$$

$$\underbrace{C_4\,H_6\,O_2}_{\text{Alcohol.}} + 2\,\underbrace{H\,C_2\,N\,O_2}_{\text{Cyanic acid.}} = \underbrace{C_8\,H_8\,N_2\,O_6}_{\text{Allophanate of ethyl.}}$$

compounds, which were prepared, however, on so small a scale as to preclude the possibility of an efficient purification.

ANALYSIS OF THE METHYL-COMPOUND.

0·1970 grm. of substance gave
0·4580 „ „ carbonic acid, and
0·1310 „ „ water,

leading to the percentage:

Carbon	63·40
Hydrogen . . .	7·38

The formula

$$C_{16}\,H_9\,N\,O_4$$

requires

Carbon	63·57
Hydrogen . . .	5·96

ANALYSIS OF THE ETHYL-COMPOUND.

0·1035 grm. of substance gave
0·2533 „ „ carbonic acid, and
0.0620 „ „ water,

leading to the percentage:

Carbon	66·74
Hydrogen , . .	6·65

The formula

$$C_{18}\,H_{11}\,N\,O_4$$

requires

Carbon	65·45
Hydrogen . . .	6.66

The results obtained in the preceding experiments, incorrect as they are, leave but little doubt in my mind respecting the existence of the two compounds in question; still the experiments will have to be repeated on a larger scale, in order to fix their existence by more characteristic numbers.

Now anilo-cyanic acid appears to exhibit a similar deportment.

I have convinced myself by analysis, that the ordinary alcohols absorb 1 equivalent of anilo-cyanic acid, giving rise to the production of the following series of compounds.

Methyl-compound . . $C_{16} H_9 N O_4 = C_2 H_4 O_2 + C_{14} H_5 N O_2$
Ethyl-compound . . $C_{18} H_{11} N O_4 = C_4 H_6 O_2 + C_{14} H_5 N O_2$
Amyl-compound . . $C_{24} H_{17} N O_4 = C_{10} H_{12} O_2 + C_{14} H_5 N O_2$

I cannot speak positively as to the existence of compounds corresponding to the second class of derivatives produced by the action of ordinary cyanic acid upon the alcohols, nor will I here venture an opinion respecting the substance formed by the action of anilo-cyanic acid and hydrated oxide of phenyl.

If we are justified in considering the urethanes as compound ethers, in which a peculiar acid, carbamic acid, pre-exists, it would follow that the preceding series would have to be regarded as the ethers of carbanilic or anthranilic acid, with whose composition they coincide.

$$\underbrace{C_6 H_7 N O_4}_{\text{Urethane.}} = \underbrace{C_4 H_5, C_2 H_2 N O_4}_{\text{Carbamate of ethyl.}}$$

$$\underbrace{C_{18} H_{11} N O_4}_{\text{Anilo-urethane.}} = \underbrace{C_4 H_5, C_{14} H_6 N O_4}_{\text{Carbanilate or anthranilate of ethyl.}}$$

I am unable to say whether these substances actually contain anthranilic acid, or whether they are only isomeric with the true anthranilic ethers. Nothing would have given me more pleasure than to pursue the investigation of these compounds farther; they present a peculiar interest, because we may expect, that under the influence of powerful removers of carbonic acid, the ethers of carbanilic acid, similarly to the cyanic ethers, will yield a series of new bases derived from aniline by the substitution of methyl, ethyl, or amyl, for 1 equiv. of hydrogen.

But unable to indulge in a more detailed study of these beautiful reactions, in consequence of want of material, I must postpone their completion until a simpler method may have been discovered of obtaining in a shorter time a larger quantity of anilo-cyanic acid. The preparation of aniline from indigo or benzole, its purification, the conversion into melaniline, the subsequent treatment of this base with cyanogen-gas, and the transformation of the resulting dicyanomelaniline into melanoximide, which, when distilled yields but a small percentage of anilo-cyanic acid—this long and complicated series of metamorphoses, have caused no small expenditure of time and labour, nor could I have found sufficient leisure to follow out the manifold ramifications of the aniline-family in its numerous and often so intricately related derivatives, whose history I have endeavoured to trace before the Society, had it not been for the valuable assistance and co-operation of Messrs. Nicholson and Abel, Assistants in the College of Chemistry. I cannot but make mention publicly of the unremitting zeal, and the remarkable experimental skill with which, during several years, these gentlemen have assisted me in the prosecution of the researches on the volatile organic bases.

Having in the preceding pages endeavoured to fix the composition and the nature of anilo-cyanic acid, we will now return once more to the circumstances under which this substance is formed, in order to trace as far as possible the connexion in which this compound stands with melanoximide, the dry distillation of which gives rise to it.

The decomposition by heat of so complex an atom as melanoximide must necessarily be a process of considerable intricacy. By the great variety of products which are simultaneously formed, carbonic oxide, carbonic acid, anilo-cyanic acid, the crystalline sublimate and the resinous residue, we are led to believe that several metamorphoses are accomplished side by side in this reaction; nor do I pretend to be in possession of a sufficient number of facts for a satisfactory explanation of all the phenomena. I offer the following remarks only as an expression of the idea which I have myself formed respecting this decomposition, leaving it to others to suggest any other interpretation of the facts which may seem to them more probable. In order to understand the effect of heat upon melanoximide, it will be necessary to premise a few details respecting the action exerted by heat upon melaniline itself.

Action of Heat upon Melaniline.

Melaniline may be exposed to the heat of boiling water without undergoing any change, between 120° C. and 130° C. the substance enters into a state of fusion, and solidifies on cooling with crystalline structure. On raising the temperature however to 150°, and then afterwards to 170° C., decomposition ensues. At the latter temperature, perfectly colourless drops of pure aniline distil over. In the commencement of this distillation no trace of ammonia is perceptible; this gas is formed however after the lapse of some time, even if the temperature be accurately kept between 150° and 170° C., and is disengaged abundantly on raising the temperature. It is almost impossible to regulate the heat, so as to evolve aniline only, without causing at the same time the elimination of ammonia. These observations show that it must be extremely difficult to obtain the residue of this operation of constant composition. This residue is a transparent, slightly yellowish, resinous, brittle mass, insoluble in water, dissolving only with difficulty in alcohol, a turbid liquid being produced which filters very slowly. It is soluble in concentrated sulphuric acid, and reprecipitated on the addition of water, in white flakes, in which the substance appears to be in an altered state. The residue obtained by heating melaniline was repeatedly analysed. I adduce the following combustions made with products obtained in different operations.

I. 0·1927 grm. of substance gave:
0·5108 „ „ carbonic acid, and
0·0980 „ „ water.
II. 0·3730 „ „ substance gave:
1·0043 „ „ carbonic acid, and
0·1710 „ „ water.
III. 0·2970 „ „ substance gave:
0·8017 „ „ carbonic acid, and
0·1360 „ „ water.
IV. 0·3185 „ „ substance gave:
0·8670 „ „ carbonic acid, and
0·1525 „ „ water.

Percentage:

	I.	II.	III.	IV.
Carbon . . .	72·29	73·43	73·62	74·24
Hydrogen . .	5·65	5·09	5·08	5·32

Among these analyses I am inclined to place most confidence in experiment I, for which the substance had been prepared with the greatest care, very little ammonia having been evolved. To ensure the absence of adhering aniline the compound had been dissolved in alcohol mixed with a few drops of hydrochloric acid, and reprecipitated by water, washed with dilute ammonia, and dried. The remainder of the combustions were made with specimens obtained by the action of heat only. The results from analysis I, the difference being assumed to be nitrogen, may be translated into the formula

$$C_{54} H_{25} N_7$$

which requires the following values:

54 equivs. of Carbon	324	72·49
25 „ of Hydrogen. . . .	25	5·59
7 „ of Nitrogen	98	21·92
1 equiv. of Melaniline-residue .	447	100·00

The simplest interpretation of this formula consists in regarding it as a compound of the aniline-mellon with 3 equivs. of aniline.

Mellon . . . . . $C_6 N_4$
Aniline-mellon . . $C_6 N_4 (C_{12} H_4) = C_{18} H_4 N_4$
$C_{54} H_{25} N_7 = C_{18} H_4 N_4 + 3\, C_{12} H_7 N.$

If this formula actually represents the composition of the body in question, its formation would be the result of the separation of 2 aniline-atoms from 3 equivs. of melaniline.

$$\begin{aligned} 3\, C_{26} H_{13} N_3 &= C_{78} H_{39} N_9 \\ 2\, C_{12} H_7\, N &= \underline{C_{24} H_{14} N_2} \\ & C_{54} H_{25} N_7 \end{aligned}$$

I have endeavoured to verify the formula in question, by determining the percentage-loss suffered by melaniline on exposure to heat. The following experiment will prove that the action of heat gives rise to a series of changes, which it is very difficult to confine to separate stages, the various periods of the process being but very indistinctly defined.

When exposed for several hours to 170° C. in an air-bath :

I. 0·2993 grm. lost . . 0·0910 grm. = 30·40 per cent
after another hour . 0·0937 „ = 31·30 „
II. 0·2980 grm. lost . . 0·0867 „ = 29·09 „
after a second hour . 0·0970 „ = 32·55 „
III. 0·6517 grm. lost . . 0·2005 „ = 30·76 „
IV. 2·1840 „ lost . . 0·682 „ = 31·22 „

On continuing the experiment ammonia was abundantly evolved, and the loss rose gradually to 35 and even to 37 per cent. From these experiments it appears that melaniline, when exposed to a temperature of 170° C. loses about 30 per cent of aniline, and that after this the decomposition enters into a new phase, ammonia being first slowly, and by degrees more rapidly evolved. The theoretical loss, required by the assumption that 3 equivalents of melaniline yield 2 equivalents of aniline, is 29·38; however, the impossibility of avoiding the evolution of ammonia altogether would explain to a certain extent, both the almost invariable excess exhibited by the latter experiments, the excess of carbon, and the deficiency of hydrogen, in several of the elementary analyses.

Accordingly without extending our considerations to the later products of the action of heat on melaniline, we are justified in assuming, that at a certain stage of the process the residue in the retort consists chiefly of a product:

$$C_{54}\,H_{25}\,N_7 = C_{18}\,H_4\,N_4 + 3\,C_{12}\,H_7\,N.$$

which may be regarded as anilo-mellon + 3 equivs. of aniline.

This mode of viewing it, is moreover supported by two analogies. The substance discovered by Liebig in the distillation of sulphocyanide of ammonium, and described under the name of melam, may be considered as a compound of 2 equivs. of mellon, and 3 equivs. of ammonia.

$$C_{12}\,H_9\,N_{11} = 2\,C_6\,N_4 + 3\,H_3\,N,$$

and it is known that this body is decomposed accordingly by heat.

Again, in subjecting chlorocyanilide to the action of heat, M. Laurent obtained a substance possessing properties very similar to those of the melaniline-residue, which from the mode of its formation, must almost certainly be

$$C_{30}\,H_{11}\,N_5 = C_{18}\,H_4\,N_4 + C_{12}\,H_7\,N,$$

i. e. anilo-mellon + 1 equiv. of aniline.

Action of Heat upon Melanoximide.

The preceding account of the action of heat upon melaniline, incomplete as it is, and insufficiently supported by experiment though it may appear, will nevertheless assist us in understanding the changes which melanoximide undergoes in the formation of anilo-cyanic acid.

Melanoximide, anilo-cyanic acid, and hydrated cyanic acid are substances of the same order. They all may be considered as having been derived from acid salts by the elimination of 4 equivs. of water.

Melanoximide is binoxalate of melaniline — 4 equivs. of water; anilo-cyanic acid, bicarbonate of aniline — 4 equivs. of water, whence the name anilo-carbimid, or in Gerhardt and Laurent's nomenclature the term *carbanile* might be used for this compound; cyanic acid or carbimide lastly is bicarbonate of oxide of ammonium — 4 equivs. of water, as illustrated by the following table, into which I introduce as second term melano-carbimide, a substance which has still to be discovered, and which would be derived from bicarbonate of melaniline in the same manner as anilo-cyanic acid and common cyanic acid may be supposed to originate from the bicarbonates of the respective bases.

Melanoximide . .	$C_{30}H_{11}N_3O_4+4HO=C_{26}H_{13}N_3, 2HC_2O_4$
Melano-carbimide .	$C_{28}H_{11}N_3O_2+4HO=C_{26}H_{13}N_3, 2HCO_3$(?)
Anilo-carbimide . Anilo-cyanic acid .	$C_{14}H_5NO_2+4HO=C_{12}H_7N, 2HCO_3$
Carbimide . . . Cyanic acid . .	$C_2HNO_2+4HO=H_3N, 2HCO_3$

Now, if we recollect that the distillation of melanoximide is attended with a very considerable evolution of carbonic oxide, it does not appear improbable that the first result of the action of heat is the actual formation of melano-carbimide, for

$$\underbrace{C_{30}H_{11}N_3O_4}_{\text{Melanoximide.}} - 2CO = \underbrace{C_{28}H_{11}N_3O_2}_{\text{Melano-carbimide.}}$$

Melano-carbimide then would yield anilo-carbimide or anilo-cyanic acid, in the same manner as melaniline on exposure to heat evolves aniline. Supposing the decomposition of the two substances to be parallel, the action of heat upon the former would be represented by the following formulæ:

$$\begin{array}{r}
3\,C_{28}H_{11}N_3O_2 = C_{84}H_{33}N_9O_6\\
2\,C_{14}H_5NO_2 = \underline{C_{28}H_{10}N_2O_4}\\
C_{56}H_{23}N_7O_2
\end{array}$$

The residue left in the retort, after the distillation of melanoximide, which in its physical characters strikingly resembles the analogous melaniline-residue, would also by its composition become a substance of similar order, it might be considered as a compound of anilo-mellon, with 2 equivs. of aniline, and 1 equiv. of anilo-cyanic acid.

Melaniline-residue	$C_{54}H_{25}N_7=C_{18}H_4N_4+2C_{12}H_7N+C_{12}H_7N$
Melanoximide-residue . . .	$C_{56}H_{23}N_7O_2=C_{18}H_4N_4+2C_{12}H_7N+C_{14}H_5NO_2$

I have analysed the residue, and the numbers obtained partially appear to confirm this view, as far as confirmation can be expected by the combustion of a compound produced in so complicated a reaction, which is neither crystalline nor volatile.

I. 0·3080 grm. of the residue gave:
0·8050 „ „ carbonic acid, and
0·1140 „ „ water.
II. 0·2070 „ „ the residue gave:
0·2885 „ „ platinum.

Percentage-composition:

	I.	II.
Carbon	71·28	
Hydrogen	4·14	—
Nitrogen	—	19·77

The above formula requires the following values:

56	equivs. of Carbon	336	71·04
23	„ „ Hydrogen	23	4·86
7	„ „ Nitrogen	98	20·72
2	„ „ Oxygen	16	3·38
		473	100·00

Accordingly the conversion of melanoximide into anilo-cyanic acid would be represented by the following equation:

$$\underbrace{3\,C_{30}\,H_{11}\,N_3\,O_4}_{\text{Melanoximide.}} = 6\,CO + \underbrace{2\,C_{14}\,H_5\,N\,O_2}_{\text{Anilo-cyanic acid.}} + \underbrace{C_{56}\,H_{23}\,N_7\,O_2}_{\text{Residue.}}$$

The compounds enumerated in the second part of this equation are, however, by no means the only products of the reaction. I have repeatedly mentioned, that together with carbonic oxide a certain quantity of carbonic acid is evolved. This gas appears to be the result of a secondary decomposition, for repeatedly, though I have determined the proportion of this acid relatively to the carbonic oxide, I have not been able to obtain concordant results, either in different experiments or in the various stages of the same operation; invariably the amount of carbonic acid is very small. A farther secondary product is the crystalline sublimate, which appears especially in the last part of the distillation when the temperature is highest; this compound which, if the heat be continued for some time, is deposited as a coating of radiated texture all over the neck of the rctort,—some crystals being even carried into the receiver,—was collected, pressed between bibulous paper and crystallized from boiling alcohol, when it was obtained in beautiful long needles. Analysis proved this substance to be perfectly pure carbanilide.

0·2880 grm. of substance gave:
0·7774 „ „ carbonic acid, and
0·1480 „ „ water,

numbers leading to the following percentage of carbon and hydrogen, which I place in juxtaposition with the theoretical values.

	Experiment.	$C_{13}\,H_6\,N\,O$.
Carbon	73·61	73·58
Hydrogen	5·71	5·66

The reactions and properties of the substance are likewise identical with those of carbanilide obtained in other processes.

In what manner is carbanilide formed in the dry distillation of melanoximide? I think that we may account for the formation of this compound in two different ways. Suppose that at the high temperature at which the process is accomplished, a certain quantity of hydrogen and oxygen is eliminated from the residue in the form of water: the water coming into contact with the vapour of the anilo-cyanic acid is decomposed, carbanilide being deposited in crystals, while carbonic acid is evolved:

$$2C_{14} H_5 N O_2 + 2HO = 2C_{13} H_6 N O + 2CO_2.$$

We have seen above that this formula is strictly verified by direct experiment, and it may be mentioned here, that the impossibility of obtaining more than traces of anilocyanic acid in the distillation of the binoxalate of melaniline is accounted for by the evolution of the 4 equivs. of water, by which this salt exceeds the composition of melanoximide, and which are sufficient to convert the whole of the anilocyanic acid into carbanilide and carbonic acid: and hence the large quantity of carbonic acid evolved and the considerable amount of carbanilide sublimed in the distillation of binoxalate of melaniline.

This reaction, then, would explain both the presence of carbonic acid and carbanilide among the products of distillation of melanoximide.

However, though it is very probable that a process like that just mentioned co-operates in the formation of carbanilide, I nevertheless believe that by far the larger quantity of the amount produced in the distillation of melanoximide is due to another reaction. In glancing once more at the expression for the residue of melanoximide we perceive that in the theoretical formula, which suggested itself, namely:

$$C_{56} H_{23} N_7 O_2 = C_{18} H_4 N_4 + 2C_{12} H_7 N + C_{14} H_5 N O_2,$$

there occur, together with that of anilo-mellon, the formulæ of aniline and anilocyanic acid. Now, when enumerating the reactions of the latter compound, I have mentioned that on adding it to aniline the mixture solidifies at once into a crystalline mass of carbanilide.

$$\underbrace{C_{14} H_5 N O_2}_{\text{Anilocyanic acid.}} + \underbrace{C_{12} H_7 N}_{\text{Aniline.}} = \underbrace{2C_{13} H_6 N O.}_{\text{Carbanilide.}}$$

It is very probable that the larger quantity of the carbanilide accompanying the anilocyanic acid, is due to a similar reaction, 1 equivalent of aniline and 1 equivalent of anilocyanic acid separating from the residue, which would thus be converted into the anilo-mellon, containing 1 equiv. of aniline, which I mentioned above, as having been obtained by M. Laurent in the action of heat upon chlorocyanilide.

Melanoximide-residue . . } $C_{18}H_4N_4, + 2C_{12}H_7N + C_{14}H_5NO_2 = C_{56}H_{23}N_7O_2$

2 equivs. of Carbanilide } $C_{12}H_7N + C_{14}H_5NO_2 = C_{26}H_{12}N_2O_2$

Laurent's Anilo-mellon } $C_{18}H_4N_4, + C_{12}H_7N = C_{30}H_{11}N_5$.

This view is partly supported by experiment. A portion of the melanoximide-residue, from which by continued strong heat every trace, both of anilo-cyanic acid and of carbanilide had been expelled, was subjected to analysis, when the following results were obtained:

0·3708 grm. of residue gave:
0·9146 ,, ,, carbonic acid, and
0·1515 ,, ,, water.

Percentage:

Carbon	67·27
Hydrogen	4·54

The formula

$$C_{30}H_{11}N_5$$

requires the following values:

30 equivs. of Carbon	108	68·97
11 ,, ,, Hydrogen	11	4·21
5 ,, ,, Nitrogen	70	26·82
1 ,, ,, Anilo-mellon and Aniline	261	100·00

It is possible that the loss of carbon may have been occasioned by incomplete combustion, these substances burning with very great difficulty; be this, however, as it may, I do not attach great importance to the analysis of these amorphous bodies produced at high temperatures, and offering no guarantee of purity and individuality, and am inclined to consider the preceding scheme of the action of heat on melaniline and melanoximide more as a probable theory than as a strict interpretation of unequivocal facts.

Having enumerated in the preceding pages the various facts concerning anilo-cyanic acid, which have been elicited during my researches, it remains now only briefly to point out some interesting relations in which this compound stands to other groups of bodies. In the beginning of this year M. Wurtz published some remarkable experiments upon the metamorphoses exhibited by the compounds of the alcohol-radicals with cyanic acid. In these several substances, exactly as in anilo-cyanic acid, the original habits of cyanic acid in its behaviour with other bodies are retained in almost every direction. We have obtained in this manner a series of compounds, of which cyanic acid is, as it were, the type:

$$\underbrace{C_2\,H\,N\,O_2}_{\text{Cyanic acid.}} \qquad \underbrace{C_2\,H\,N\,O_2\,(C_2\,H_2)}_{\substack{\text{Methylo-cyanic acid, or}\\ \text{Cyanate of Methyl.}}} \qquad \underbrace{C_2\,H\,N\,O_2\,(C_4\,H_4)}_{\substack{\text{Ethylo-cyanic acid, or}\\ \text{Cyanate of Ethyl.}}}$$

$$\underbrace{C_2\,H\,N\,O_2\,(C_{10}\,H_{10})}_{\substack{\text{Amylo-cyanic acid, or}\\ \text{Cyanate of Amyl.}}} \qquad \underbrace{C_2\,H\,N\,O_2\,(C_{12}\,H_4)}_{\substack{\text{Anilo-cyanic acid, or}\\ \text{Cyanate of Phenyl.}}}$$

All these substances are capable of fixing directly 1 equiv. of ammonia, a series of compounds being produced analogous in composition to urea:

$$\underbrace{C_2\,H_4\,N_2\,O_2}_{\text{Urea.}} \qquad \underbrace{C_2\,H_4\,N_2\,O_2\,(C_2\,H_2)}_{\text{Methylo-urea.}} \qquad \underbrace{C_2\,H_4\,N_2\,O_2\,(C_4\,H_4)}_{\text{Ethylo urea.}}$$

$$\underbrace{C_2\,H_4\,N_2\,O_2\,(C_{10}\,H_{10})}_{\text{Amylo-urea.}} \qquad \underbrace{C_2\,H_4\,N_2\,O_2\,(C_{12}\,H_4)}_{\text{Anilo-urea, Carbamide-carbanilide.}}.$$

When in contact with water, 2 equivs of the various cyanic acids assimilate 2 equivs. of water, 2 equivs. of carbonic acid being evolved. In this case compounds are formed which are analogous to carbamide, urea appearing here as bicarbamide:

$$\underbrace{H_2\,N,\,CO;\;N\,H_2,\,CO}_{\text{Urea, bicarbamide.}} \qquad \underbrace{H_2\,N,\,CO\,(C_2\,H_2)}_{\text{Methylo-carbamide.}} \qquad \underbrace{H_2\,N,\,CO\,(C_4\,H_4)}_{\text{Ethylo-carbamide.}}$$

$$\underbrace{H_2\,N,\,CO\,(C_{10}\,H_{10})}_{\text{Amylo-carbamide.}} \qquad \underbrace{H_2\,N,\,CO\,(C_{12}\,H_4)}_{\substack{\text{Anilo-Carbamide, Carbanilide,}\\ \text{Phenylo-carbamide.}}}.$$

Lastly, when treated with the alkalies, 2 equivs. of water are fixed; a series of conjugated ammonias being formed while carbonic acid is eliminated:

$$\underbrace{H_3\,N}_{\text{Ammonia.}}\,;\ \underbrace{H_3\,N\,(C_2\,H_2)}_{\substack{\text{Methyl-ammonia,}\\ \text{Methylamine.}}}\,;\ \underbrace{H_3\,N\,(C_4\,H_4)}_{\substack{\text{Ethyl-ammonia,}\\ \text{Ethylamine.}}}\,;\ \underbrace{H_3\,N\,(C_{10}\,H_{10})}_{\substack{\text{Amyl-ammonia,}\\ \text{Amylamine.*}}}\,;\ \underbrace{H_3\,N\,(C_{12}\,H_4)}_{\substack{\text{Phenyl-ammonia,}\\ \text{Phenylamine,}\\ \text{Aniline.}}}.$$

The preceding synopsis shows the analogy of these various compounds in a sufficiently perspicuous light; it requires no farther comment. I will observe only that these analogies begin to exhibit the alcoholic nature of phenole in a very forcible manner. In fact in anilo-cyanic acid, we add a new member to the phenole-group, in which already some of the most important terms of the common alcohol-series are represented.

Alcohol	$C_4\,H_5\,O,\ HO$	Phenole	$C_{12}\,H_5\,O,\ HO$
Sulphethylate of barium	$C_4\,H_5\,SO_4,\ Ba\,SO_4$	Sulphophenate of barium	$C_{12}\,H_5\,SO_4,\ Ba\,SO_4$
Chloride of ethyl	$C_4\,H_5\,Cl$	Chloride of phenyl	$C_{12}\,H_5\,Cl$ (?)
Cyanide of ethyl Metacetonitrile	$C_4\,H_5\,Cy = C_6\,H_5\,N$	Cyanide of phenyl Benzonitrile	$C_{12}\,H_5\,Cy = C_{14}\,H_5\,N$
Metacetic acid	$C_6\,H_6\,O_4$	Benzoic acid	$C_{14}\,H_6\,O_4$
Metacetic ether	$C_4\,H_5\,C_6\,H_5\,O_4$	Benzoate of phenyl	$C_{12}\,H_5\,C_{14}\,H_5\,O_4$
Cyanate of ethyl Ethylo-cyanic acid	$C_4\,H_5,\ C_2\,N\,O_2$	Cyanate of phenyl Anilo-cyanic acid	$C_{12}\,H_5\,C_2\,N\,O_2$
Ethylo-carbamide Carbethylamide	$C_5\,H_6\,N\,O$	Phenylo-carbamide Carbanilide	$C_{13}\,H_6\,N\,O$
Ethylo-urea	$C_6\,H_8\,N_2\,O_2$	Anilo-urea	$C_{14}\,H_8\,N_2\,O_2$
Ethylammonia Ethylamine	$C_4\,H_7\,N$	Phenylamine Aniline	$C_{12}\,H_7\,N$

The preparation of anilo-cyanic acid being, as mentioned above, attended with considerable difficulty, the new aspect under which this compound appears, when considered as cyanate of phenyl, could not but induce me to try whether it might not be formed in the same manner as the alcohol-cyanates. The latter compounds and the corresponding aniline-term, although, as we have seen, perfect analogues, have been obtained by very different processes. The alcohol-cyanates are formed, like so many other compound ethers, simply by distilling a mixture of a sulphethylate and a cyanate; indeed these substances form the starting point of the alcohol-bases, while in the case of cyanate of phenyl or anilo-cyanic acid, this body has to be constructed, as it were, by very complicated reactions from the phenole-base itself.

Cyanate of phenyl, however, is not produced under those circumstances which give rise to the formation of cyanate of methyl, ethyl, or amyl. I have in vain distilled a mixture of cyanate of potash with sulphophenate of baryta; the smallest trace of anilo-cyanic acid, would have been at once detected by the nose; it is not formed in this reaction.* Incidentally to this experiment I have distilled sulphophenate of baryta with cyanide of potassium; this reaction might have given rise to the formation of cyanide of phenyl or benzonitrile, a transformation, which appeared of some interest, inasmuch as it would have enabled us to reach from phenole upwards to benzoic acid, in the same manner as we now step from one alcohol-family through the cyanide or nitrile into the acid term of the family following next on the scale of organic compounds; however, in distilling sulphophenate of baryta with sulphethylate of potash no benzonitrile is obtained.

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* M. Wurtz assigns to this compound the term valeramine, but I think amylamine is a more appropriate appellation.

The impossibility of obtaining cyanate and cyanide of phenyl in the same manner as the corresponding terms in the methyl-, ethyl-, and amyl-series, sufficiently shows that the properties of the phenyl-alcohol differ in many respects from those of the alcohols $C_n H_{(n+2} O_{2},)$ (*n* representing the numbers 2, 4, 6, &c.); we might in fact adduce a variety of other dissimilarities; but we have to recollect that phenole is no homologue but only an analogue of common alcohol, the number of carbon-equivalents considerably exceeding that of the hydrogen-atoms, while the above alcohols, as indicated by the general formula, invariably contain an excess of hydrogen.

Notwithstanding these discrepancies it may not be useless to bear in mind the alcoholoid habit of the phenole-family, were it only that its various derivations might assist us in increasing the sources, so scanty at present, of alcohol formation. One of the most definite processes effecting the production of phenole is the exposure of salicylic acid to heat or the action of alkaline earths upon it. Now, we know from M. Strecker's experiments, a continuation of which is impatiently expected by chemists, that the deamidation of glycycin (glycycol), sarcosin and leucin gives rise to a series of acids containing 6 equivalents of oxygen, and standing to the ordinary

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* I may mention here some other unsuccessful experiments, which I have tried in order to obtain anilo-cyanic acid. This compound contains the elements of anthranilic acid or salicylamide — 2 equivs. of water,

$$\underbrace{C_{14}\,H_7\,N\,O_4}_{\substack{\text{Anthranilic acid.}\\\text{Salicylamide.}}} - 2\,HO = \underbrace{C_{14}\,H_5\,N\,O_2}_{\text{Anilo-cyanic acid.}}$$

I have distilled anthranilic acid and salicylamide with anhydrous phosphoric acid, but no anilo-cyanic acid is produced, the action going evidently too far. In the case of anthranilic acid nearly the whole substance is charred.

by elimination of	Compounds produced from Acid Salts by elimination of 4 equivs. of Water.	
IDOGEN-ACIDS.	IMIDES.	ANILIMIDES or ANILES.
: or Anthranilic acid '$_3$; C_{12} H_6 N, CO.	Cyanic acid H N, 2 CO.	Anilo-cyanic acid (carbanile) C_{12} H_5 N, 2 CO
.. ..	Sulphocyanic acid H N, 2 CS.	
)xanilic acid ; C_{12} H_6 N, C_2 O_2.		
.. ..	Benzimide H N, 2 C_{14} H_5 O_2.	
:inanilic acid ; C_{12} H_6 N, C_4 H_2 O_2.	Succinimide H N, 2 C_4 H_2 O_2	Succinanile C_{12} H_5 N, 2 C_4 H_2 O_2
eranilic acid ; C_{12} H_6 N, C_8 H_6 O_2.		
alanilic acid ; C_{12} H_6 N, C_8 H_2 O_2.	Phtalimide H N, 2 C_8 H_2 O_2	Phtalanile C_{12} H_5 N, 2 C_8 H_2 O_2
›horanilic acid ; C_{12} H_6 N, C_{10} H_7 O_2.	Camphorimide. H N, 2 C_{10} H_7 O_2	Camphoranile C_{12} H_5 N, 2 C_{10} H_7 O_2.
)hanilic acid ; C_{12} H_6 N, SO_2.		

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alcohols in a relation similar to that existing between salicylic acid and phenole. It would be interesting to ascertain whether these acids do not exhibit a similar deportment, and whether a passage cannot be effected in this manner from glycycin into the methyl-, from sarcosin into the ethyl-, and from leucin into the amyl-series.

VII.—ACTION OF ANHYDROUS PHOSPHORIC ACID ON VARIOUS ANILINE-SALTS AND ANILIDES.

The salts of oxide of ammonium, both neutral and acid, when subjected to the influence of heat, lose either 2 or 4 equivs. of water; four classes of compounds being thus produced; neutral oxalate of oxide of ammonium, by the loss of 2 equivs. of water, becomes oxamide, while by the elimination of 4 equivs. of water, cyanogen or oxalo-nitrile is formed. Binoxalate of ammonia, when losing 2 equivs. of water, is converted into oxamic acid; a compound arising from the binoxalate by the loss of 4 equivs. of water, has not as yet been formed; this term, however, is found to be represented among the derivatives of the ammonia-salts of various other acids, e. g., of camphoric and pthalic acids, camphorimide and pthalimide being bicamphorate and biphtalate of ammonia — 4 equivs. of water. We may thus distinguish as derived from the ammonia-salts by loss of water:

1. Amides.
2. Nitriles.
3. Amidogen-acids.
4. Imidogen-compounds. (Imides.)

The researches of the last three years have shown that in the salts of organic bases resembling those of ammonia in so many respects, the analogy extends also to the faculty of giving up a certain amount of water when subjected to the action of heat. The experiments from which our knowledge respecting this deportment of organic bases is derived, have been chiefly performed with aniline, and the extent to which the various terms are even now represented in the aniline-series could not perhaps be better illustrated than by the following synoptical table, in which I have placed the derivatives of ammonia and of aniline side by side. (*See* Table).

A glance at this table shows that both the amides and the amidogen-acids are pretty numerously represented in the aniline-series. Less frequently in this series do the imidogen-compounds appear, of which, however, the number is on the increase, the preceding paper having pointed out the existence of a new member both in the aniline- and melaniline-family (anilocyanic acid and melanoximide). There is only one column in this table in which the spaces for the aniline-terms are altogether vacant, *i. e.*, the column for the anilo-nitriles; there is no compound known which is derived from a neutral aniline-salt by the elimination of 4 equivs. of water.

The following experiments were undertaken in order to fill up this gap. My attention was first directed to the dehydration of oxalate of aniline. This salt, as is well known, when subjected to dry distillation, loses, like the corresponding ammonia-compound, 2 equivs. of water, oxanilide being formed. The removal of two additional water-equivalents would have given rise to the formation of a compound corresponding to cyanogen or oxalonitrile. Such a compound, anilocyanogen, aniloxalonitrile, $C_{14} H_4 N_2 = Cy C_{12} H_4$, I have tried to obtain by the various methods which have been successfully employed in the formation of cyanogen, from oxalate of ammonia. Oxalate of aniline, as well as oxanilide, were repeatedly subjected to rapid distillation, either alone, or with anhydrous baryta, with protochloride of zinc, or with anhydrous phosphoric acid. The results of these experiments were far from what I expected. Oxanilide when distilled alone, was volatilized almost without decomposition, only an exceedingly small quantity of an odorous oil being produced. In the treatment with anhydrous baryta, aniline chiefly is evolved; while by the action of protochloride of zinc and of anhydrous phosphoric acid, nearly the whole mass is charred, carbonic acid and carbonic oxide being evolved at the same time. In these latter processes, however, and more particularly in the distillation of oxanilide with anhydrous phosphoric acid, the oil which I mentioned before, is generated in somewhat larger quantity, a crystalline deposit being formed at the same time in the neck of the retort.

At the time when I first performed these experiments, I imagined that the odorous compound in question was the cyanogen of the aniline-series, derived from oxalate of aniline in the same manner as cyanogen itself arises from oxalate of oxide ammonium:

$$H_3 N,\ H C_2 O_4 - 4 HO = C_2 \qquad N.$$
$$C_{12} H_7 N,\ H C_2 O_4 - 4 HO = C_{14} H_4 N.$$

But unable to procure, even by the sacrifice of several ounces of oxanilide, a quantity of this compound sufficient to establish its nature, either by analysis or the study of its reactions, I was obliged to desist at the time from a farther prosecution of the inquiry.

It was not until I had investigated the derivatives of dicyanomelaniline, that I became acquainted with the actual composition of the body in question. But having once obtained anilocyanic acid in the destructive distillation of melanoximide, there was no difficulty in recognizing that the compound formed in treating oxanilide with anhydrous phosphoric acid, is nothing but the same anilocyanic acid. The odour could not leave the slightest doubt upon this point, but small though the quantity of oil was which I obtained in distilling oxanilide, it sufficed to repeat with this product the principal reactions of anilocyanic acid, which I have enumerated in the preceding paper; so that I have not the slightest hesitation in asserting their identity, although I cannot offer the conclusive test of a combustion.

The exceedingly small quantity of anilocyanic acid formed in this process, quite disproportionate to the amount of oxalate of aniline or oxanilide employed, shows that its formation is by no means due to a regular reaction, but to a complicated decomposition, in which the largest quantity of the oxanilide is actually destroyed, a circumstance which is clearly proved by the large quantity of charcoal separated in the process. The crystals in the neck of the retort are nothing but carbanilide mixed with a small quantity of oxanilide, which has escaped decomposition. The formation of carbanilide is simply due to the simultaneous evolution of some aniline, which meeting with the vapour of anilocyanic acid, gives at once rise to the production of this compound.

The formation of anilocyanic acid and carbanilide is supported, moreover, by the products arising from the destructive distillation of oxamide, in which, together with carbonic oxide, cyanogen and hydrocyanic acid, we invariably observe cyanic acid and ammonia, which we find again in the neck of the retort in the form of urea (bicarbamide).

It is not difficult to see in what manner anilocyanic acid is derived from oxanilide, these two substances differing only by 1 eq. of hydrogen, which the latter contains in excess.

$$\underbrace{C_{14}\,H_6\,N\,O_2}_{\text{Oxanilide.}} - H = \underbrace{C_{14}\,H_5\,N\,O_2}_{\text{Anilocyanic acid.}}.$$

The removal of this hydrogen may be effected in various ways; we may suppose, e. g., that it is consumed in the regeneration of an equivalent of aniline:

$$2\,\underbrace{C_{14}\,H_6\,N\,O_2}_{\text{Oxanilide.}} = \underbrace{C_{14}\,H_5\,N\,O_2}_{\text{Anilocyanic acid.}} + \underbrace{C_{12}\,H_7\,N}_{\text{Aniline.}} + 2\,CO.$$

There must, however, be other modes, for if aniline and anilocyanic acid were eliminated in equal equivalents, the whole would be obtained in the form of carbanilide, no free anilocyanic acid being perceptible.*

The chief result then of the preceding experiments, is that under those circumstances which induce the elimination of 4 equivs. of water from an ammonia-salt, no corresponding aniline-compound is produced.

I have performed a series of perfectly similar experiments with benzoate of aniline and benzanilide. Under the influence of phosphoric acid or protochloride of zinc, which so readily effect the conversion of benzoate of ammonia or benzamide into benzonitrile, the corresponding aniline-compounds are altogether charred. In no manner did I succeed in obtaining the aniline-term, representing benzonitrile.

What then, may we ask, is the reason why aniline, which so faithfully imitates all the habits of ammonia, refuses to follow its example with respect to the formation of the nitriles? The answer to this question involves a careful consideration of the constitution of aniline and the analogous bases.

In a former paper† I have given a synopsis of all the facts, supporting the view of Berzelius, that the organic bases are conjugated ammonia-compounds, in which ammonia pre-exists. According to this view, which was in perfect accordance with all the observations which had then been made, aniline is represented by the formula:

$$H_3\,N,\,(C_{12}\,H_4),$$

and an aniline-salt, e. g., the oxalate, by the formula:

$$H_3\,N,\,(C_{12}\,H_4)\,H\,C_2\,O_4.$$

This formula gives no satisfactory answer to the above question. There is no comprehensible reason why the oxalate of ammonia in the aniline-salt should not be deprived of its four equivalents of water, and why the residuary cyanogen should not be associated with the usual adjunct.

We possess, however, another view respecting the nature of the organic bases. According to Liebig's ideas, these substances have to be considered as amidogen-compounds. In regarding aniline as an amidogen-compound, the question appears under a perfectly different light. In representing aniline by the formula:

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* In the paper on cyaniline (Chem. Soc. Qu. J., I. 159). I have mentioned that the remarkable odour (of anilocyanic acid) is strongly evolved in the treatment of this base with acids. This is now intelligible, if we recollect that the same reaction gives rise to the formation of oxanilide.

† Chem. Soc. Qu. J. I. 285.

$$(C_{12}\,H_5)\,H_2\,N,$$

and the aniline-salts, e. g. the oxalate and binoxalate, by the formulæ:

$$(C_{12}\,H_5)\,H_3\,N,\,H\,C_2\,O_4,$$
$$(C_{12}\,H_5)\,H_3\,N,\,H\,C_2\,O_4,\,H\,C_2\,O_4,$$

we may understand without difficulty that under the influence of dehydrating agents, the latter may lose either 2 or 4 equivs. of water, (formation of anilidogen-acids, or imidogen-compounds); we understand farther, that the neutral salt may lose 2 equivs. of water (in the formation of oxanilide), but we see with the same facility, that the elimination of 4 equivs. of water from the neutral salt is altogether impossible, without the destruction of the term $C_{12}\,H_5$ (phenyl) replacing the third equiv. of hydrogen in the ammonia, only 3 equivs. of hydrogen being without the parenthesis.

It is probable that considerations like those developed in the preceding pages, will materially assist in the elaboration of more rational views respecting the constitution of the organic bases. The apparent impossibility of obtaining an anilocyanogen, throws some doubt on the pre-existence of ammonia in aniline. It is probably more in conformity with truth to consider aniline as a substitution-product, as ammonia, in which part of the hydrogen is replaced by phenyl, and this opinion may perhaps meet with the approbation of the Society, if I mention that a series of researches on the action of the bromides of the alcohol-radicals on aniline and on ammonia have enabled me actually to replace the basic hydrogen of these substances, equivalent for equivalent, by the alcohol-radicals, and to produce in this manner a numerous series of new alkaloids which appear to admit of no other mode of interpretation.

Nov. 19, 1849.

Thomas Graham, Esq., Vice-President in the Chair.

The Donations announced were:

"On the use of the Blow-pipe," by Professor Plattner. Translated by J. S. Muspratt, Ph.D., from the Translator.

"Taylor's Calendar of the Meetings of Scientific Bodies for 1849—1850," from the Author.

"The new and admirable case of settinge of lime, 1601," being a reprint, from Mr. J. C. Nesbitt.

The following papers were read:

XXXI.—*On the Waters of the Dead Sea.*

By MR. THORNTON J. HERAPATH AND
WILLIAM HERAPATH, ESQ., F.C.S.

PRESIDENT OF THE BRISTOL PHILOSOPHICAL AND LITERARY SOCIETY, AND LECTURER ON CHEMISTRY AND TOXICOLOGY AT THE BRISTOL SCHOOL OF MEDICINE, &c. &c.

THE Dead Sea, or as it is called by the Arabs, Bahr Lout (Lot's Sea), though somewhat insignificant in size, has, nevertheless, in consequence of the extraordinary physical character of its waters, and the awe and mystery which ancient tradition has thrown around its history, attracted the attention of mankind from time immemorial. Under the several appellations of the "Salt Sea," (Num. xxxiv, 3; Deut iii, 17; Josh. xv, 5); the "Sea of the Plains," (Deut. iv, 49); and the "East Sea," (Ezek. xlvii, 18; Joel ii, 20), frequent mention of it is to be met with in the Holy Scriptures; and, in fact, it is now supposed to occupy the site of the cities of Sodom and Gomorrah, the destruction of which, by the wrath of the Almighty, is so graphically described in the eighteenth chapter of Genesis. In the works of the Greek and Roman authors, again, it is often referred to by the name of "Lacus Asphaltites," or the "Bituminous Lake," and many remarks upon the exceeding saltness of its waters, and the sterility and desolate aspect of its shores, are to be found in the pages of Tacitus and Pliny.*

The lake itself, as is well known to every person acquainted with geography, is situated in the south of Palestine, at no great distance from Jerusalem, and is principally supplied by that venerated stream, the Jordan. Its breadth, it would appear from a recent survey, undertaken by Messrs. Moore and Beke, in 1837, is about nine miles, and its length, according to the same authorities, is thirty-nine or forty miles. The latter, however, is found to vary considerably at different times of the year, according to the extent of the influx derived from the Jordan and other tributary rivers.* The bottom, these gentlemen found to be rocky and of very unequal depth, ranging 120, 180, 240 and even 480 feet, all within the distance of a few yards. With regard to its geological situation, the lake lies in a deep basin, of an irregular oblong figure, and is surrounded by steep cliffs of naked limestone, which, on the western side, run up to the height of 1,500, and on the eastern to 2,500 feet above the level of the water.

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* Tacitus, lib. v, Hist. cap. VI; Strabonis Geogr. Plinii, lib. v, cap. XV and XVI; see also vol. II, p. 1107.

On the surface of the sea, there is often found floating an immense quantity of asphaltum, which is generally carried by the influence of the wind to the western and southern shores, where it is carefully collected by the Arabs, who use it as pitch and sell it for medicinal purposes. It was this substance which seems to have been employed in ancient times, by the Egyptians, to a very great extent, for embalming bodies. There are also several mines of sulphur and rock-salt in the sides of the mountains on the western coast, which not only afford supplies of those useful articles to the Arabs, but even to the inhabitants of the Holy City. Indeed, many travellers have stated that the remarkable saltness of the waters is principally occasioned by the existence of similar saline formations at the bottom of the sea. So deeply, in fact, is the surrounding soil impregnated with this ingredient, that few or no vegetables will grow there, and it is from this circumstance, combined with the absence of all animal life, either in the waters or on the shore, that recent travellers have conferred upon the lake the name "Mare Mortuum," or the Dead Sea.

The water, like that of the sea, is stated to be of a deep blue colour, shaded with green; but it is considerably more salt, and intolerably nauseous and bitter to the taste. Rae Wilson, who wrote some years ago, describes it to be not unlike the Harrowgate waters in taste and smell, but more disagreeable; although it approached more closely in character to bilge-water. Its specific gravity is so great, that it is almost impossible for a man to sink in it; persons who are entirely unacquainted with swimming, can lie, sit, or swim in it with the greatest ease. Josephus relates that the Emperor Vespasian, for the sake of an experiment, caused certain men to be thrown into this sea, with their hands and feet bound with cords, and they floated on the surface.

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* It is more than probable that its dimensions have become contracted in modern times, as, if we may believe Josephus, at the period when he wrote, it was 72 miles long by 18 broad.

Bathers in this lake, however, experience a curious sensation of the eyes, which has been described by Mr. Legh as temporary blindness; and upon getting out of the water, evaporation proceeds only very slowly, leaving a thick oily incrustation of salt adherent to the skin, which remains for many days, as it is impossible to remove it completely, even by repeated ablution.

Notwithstanding, however, that the most obvious peculiarities of the water of the Dead Sea have been known and recognized for many ages, it has only been in comparatively modern times that scientific men have attempted its chemical examination. Within the present century, Lavoisier, Marcet, Klaproth, Gay-Lussac, Gmelin, and Apjohn have each analysed it.

The celebrated Lavoisier experimented upon it in conjunction with his no less renowned countrymen MM. Macquer and Sage,* in the year 1778 (*vide* Table). At that early period, however, analytical chemistry had not attained to such a degree of accuracy as that of which it is now susceptible, and consequently there is little or no doubt but that they must have overlooked many of the most important constituents. The same remarks, apply to all of the three analyses which follow next in the series; namely, that of Dr. Marcet in 1807, of Professor Klaproth, and of M. Gay-Lussac in 1818. The former of these analysts was, moreover, inconvenienced by the smallness of the quantity which he operated upon, which did not amount to more than an ounce and a half.

The great differences which are to be observed in Professor Klaproth's numbers (*vide* Table) as compared with those obtained by the other two experimenters, according to Dr. Marcet, are occasioned by that chemist having employed too low a temperature for the purpose of desiccation.

The last two analyses of these waters, that have been published, are those by Professor Gmelin, of Tübingen, and by Dr. Apjohn, of Dublin. The former appeared in the year 1826, and the latter in 1837; they are given in the synoptical table at the end.†

On comparing the results of these six analyses, it will be seen, that in no two instances do they agree either in the proportion or composition of the contained salts. The two latter, by Gmelin and Apjohn, are evidently the ones most to be depended upon, for the reasons already stated; but even between these, many very great differences occur. The lower specific gravity of Apjohn's specimen, which was occasioned by its having been collected at the close of the rainy season, and at about half a mile's distance from the mouth of the Jordan, may, it is true, partly account for these: but it certainly will not explain the absence of the chlorides of aluminum and ammonium, both of which were found by Gmelin, the former particularly, in rather considerable quantity. For these reasons, it was therefore obvious that another analysis of the waters, performed with all the care and precautions that are now usually employed in this species of investigation, was absolutely necessary, in order that we might be enabled to determine which of the above analyses was the most trustworthy, or to point out the cause or causes which led to the discrepancies observed. Consequently, when Mr. C. J. Monk, (son of the venerable Bishop of Gloucester and Bristol), who has recently returned from a long journey in Syria and the Holy Land, kindly offered to place at our disposal for this purpose a bottle of the water, we most willingly acceded to his proposal, with what result the following pages must testify.

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* Mémoires de l'Académie des Sciences, p. 69.

† An analysis by Dr. R. Marchand appeared this year in the Journ. für prakt. Chem. B. XLVII. 353.—ED.

The specimen so presented to us was collected by Mr. Monk, himself, on the 10th of March last, near the north-western extremity of the lake, about half a mile from the spot where the Jordan enters, but quite apart from all direct influence arising from the stream of fresh water which flows into it.

I. PRELIMINARY EXAMINATION.

The water was perfectly clear and colourless, and did not deposit any crystals on standing in closed vessels, even when cooled considerably below its ordinary temperature. Its taste, as we have before observed, was intensely bitter and nauseous, and when swallowed, even in small quantity, it produced a sensation bordering upon sickness. It possessed no unpleasant odour. Its specific gravity, at 66° F., was 1·17205. The boiling-point, as determined in a glass vessel, with the barometer at 29·74 inches and the thermometer at 47·75°, was 221·75° F.* It did not exert any definite reaction upon either blue or reddened litmus-paper, proving the absence of all uncombined acid and carbonated alkali; neither did it in the slightest degree affect acetate-of-lead-paper, as from Rae Wilson's statement we should have expected it. Only the slightest perceptible opalescence was produced in it upon boiling, or on the addition of an ammoniacal solution of chloride of calcium, when, in the latter case, care was taken to add previously a sufficient quantity of muriate of ammonia to prevent the precipitation of the magnesia. Consequently, only the faintest traces of carbonic acid or carbonate of lime were present.

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* Dr. Apjohn found that of his specimen to be 221°.

The chloride of gold test of Dupasquier gave unmistakeable proofs of the existence of an abnormal proportion of organic matter. Other reagents showed that it likewise contained magnesia or magnesium, lime, alumina, the oxides of iron and manganese, soda, potash and ammonia; also chlorine, bromine, and sulphuric acid, with traces of silica, bitumen, and iodine. The latter occurred only in exceedingly minute proportion.

II. QUANTITATIVE ANALYSIS.

A. Determination of the entire amount of saline ingredients.

Great care was requisite in this part of the investigation in order to avoid loss from the evolution of hydrochloric acid, by the decomposition of the earthy and metallic chlorides at the high temperature to which it was necessary to expose the saline residue previously to weighing. This source of error was obviated by mixing a known weight of perfectly pure and anhydrous carbonate of soda with the water, prior to evaporation.

	Weight of water taken.	$\mathrm{Na\,O, CO_2}$ employed.	Saline residue obtained.	True percentage of salts.
I.	1281·9296 grs.	229·53	537·727	24·03998
II.	1709·2395 „	306·04	717·256	24·05668
			Mean .	24·04833*

B. Estimation of the Organic Matters.

The saline residue from the first experiment, which had been dried at a temperature of 350° F., was repeatedly extracted with boiling water, and the solution evaporated to dryness. The dried matters which remained behind were then finely powdered, again dried for many hours at 350° F., and afterwards heated to redness. The loss amounted to 0·792=0·06173 per cent of organic matters in the water.

The residue from the second experiment (*A.* II.) was employed in testing for the organic acids; not the slightest trace, however, of crenic or apocrenic acid could be detected.

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* Even this determination, however, it will be hereafter seen, is somewhat below the truth, on account of the sublimation of a small quantity of sesquicarbonate of ammonia, produced by the action of the carbonate of soda on the chloride of ammonium contained in the water.

C. Examination for Nitric Acid.

In this attempt we made use of the test which has been lately described by M. Lassaigne.* A known quantity of the water was evaporated to dryness. The salts thus obtained were then reduced to a fine powder, and treated several times in succession with boiling alcohol, sp. gr. 0·8010, until everything soluble in that menstruum was extracted. The alcoholic solution having been then introduced into a retort, and the greater part of the alcohol removed by distillation, the remainder was evaporated to the consistence of a syrup, and treated with a large excess of recently-precipitated tribasic-phosphate of silver. A moderately large quantity of water was then added, and the chloride, bromide and excess of phosphate of silver separated by filtration. Upon testing the filtered solution with an alkaline chloride, only a very slight degree of opacity was produced, and even this, in all probability, was caused by the presence of a small quantity of the phosphate of silver, which is known to be not perfectly insoluble in water.

It may be observed, that in a comparative experiment, undertaken in order to ascertain the value of this test, we could readily detect and estimate quantitatively the nitric acid, when 0·01 gr. of nitrate of potash was added to 970 grs. of a mixture of chloride of sodium and sulphate of soda.

The same negative results as to the presence of nitric acid in the water were obtained by our own process, described in the last number of the Quarterly Journal of the Society (No. VII. p. 203).

D. Determination of the Sulphuric Acid, Chlorine, and Bromine.

a. 1709·2395 grs. of the water were precipitated by nitrate of baryta; we obtained of sulphate of baryta 2·013 grs. = 0·68235 gr. of sulphuric acid = 0·039921 per cent.

b. The filtered solution was acidified with nitric acid, and an excess of nitrate of silver added; the mixed precipitate of chloride and bromide of silver produced, weighed 1060 784 grains. This matter was then heated to redness in a current of dry chlorine gas, and the loss of weight noted; it amounted to 2·004 grs. It therefore contained of:

			Percentage of water.
Chlorine . .	262·97838 grs.	=	15·44420
Bromine . .	3·72041 ,,	=	0·21767

We likewise examined the water for iodine, both by the ordinary test of nitrate of palladium, and also by that of starch and sulphuric acid, adopting the precautions mentioned by Dr. Cantù;* but only very faint and doubtful traces could be discovered.

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* Comptes Rendus, August 13. 1849, also see Chem. Gaz. vol. VII. p. 363.

E. Estimation of the Alumina and the Oxides of Iron and Manganese.

The alumina was precipitated in the first instance with the iron and manganese as sulphurets, the latter were afterwards peroxidized and separated from each other in the ordinary manner.

1709·2395 grains of the water gave a precipitate of the three oxides, which weighed 0·465 gr. This contained of:

			Per cent of water.
Fe_2O_3 . .	0·029	=	0·001697
Mn_2O_3 . .	0·064	=	0·003745
Al_2O_3 . .	0·379	=	0·022174

F. Estimation of the lime and magnesia.

Water taken.	Carbonate of Lime.		Lime.		Per centage in water.
1709·2395	38·320 grs.	=	21·45903	=	1·255474
	Pyrophosphate of magnesia.		**Magnesia.**		
	154·820 grs.	=	56·64233	=	3·313890

G. Estimation of the potash and soda.

Water taken.	Mixed alkaline chlorides.	Potasssio-chloride of platinum.		Chloride potassium.
				20·8075 grs.
				Chloride sodium.
1709·2395	227·792 grs.	67·627	=	206·9845 grs.

This quantity of water, therefore, contained of

Potash . . 13·141542 = 0·768853 per cent.
Soda . . . 110·391596 = 6·458519 „

H. Estimation of the ammonia.

2563·8590 grs. of the water distilled with an excess of caustic potash yielded ammonio-chloride of platinum 0·641 gr. = 0·04591 gr. of ammonia = 0·001791 per cent in the water.

Now upon collecting together the above numbers, it will be seen that 100 parts of the water of the Dead Sea yielded, of

Organic matter (*B*) . . .	0·061730
Sulphuric acid (*D. a.*) . . .	0·039921
Chlorine (*D. b.*)	15·444200
Bromine	0·217670
Peroxide of iron (*E*) . . .	0·001697
Sesquioxide of manganese . .	0·003745
Alumina	0·022174
Lime (*F*)	1·255472
Magnesia	3·313890
Potash (*G*)	0·768853
Soda	6·458519
Ammonia (*H*)	0·001791

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* Raccolta Fisico-Chemica Italiana, No. XXVIII. 1848. See also Chem. Gaz. vol. VI. p. 394.

Consequently its true composition will be:

Chloride of calcium	2·455055 per cent
Chloride of magnesium	7·822007 ,,
Bromide of magnesium	0·251173 ,,
Iodide of magnesium	doubtful traces
Chloride of sodium	12·109724 per cent
Chloride of potassium	1·217350 ,,
Chloride of ammonium	0·005999 ,,
Chloride of aluminum	0·055944 ,,
Chloride of manganese	0·005998 ,,
Chloride of iron	0·002718 ,,
Organic matter (nitrogenous)	0·061730 ,,
Nitric acid	very doubtful traces
Carbonate of lime	faint trace*
Sulphate of lime	0·067866 per cent
Silica	traces
Bituminous matter	ditto
	24·055564
Total amount of salt as determined by actual experiment	24·048330†

We shall refrain from entering upon any comparison of our analysis with those previously published; but shall content ourselves with calling the attention of the members to the subjoined synoptical table; a glance at which will enable them to arrive at a much more correct idea as to the correspondence of the several results than any amount of words would do.

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* After the above analysis was concluded, a further proof of the existence of carbonate of lime in the water was obtained in the following manner. Upon casually examining the sides of the empty bottle by transmitted light, a very small quantity of a grey flocculent substance was seen adhering to the inner surfaces; and this, being separated by means of a clean caoutchouc washer and a few drops of distilled water, was found to weigh 0·029 gr. (per quart). When examined chemically, it effervesced upon the addition of a diluted acid, and the solution was precipitated by oxalate of ammonia, &c., in the same manner as lime. No effect was produced either by ammonia, or the triple phosphate of soda and ammonia; it therefore did not contain alumina, oxide of iron, or magnesia.

† Close as is the approximation between these two determinations, yet, if we take into consideration the small loss which must naturally have taken place in the second instance from the evolution of the ammoniacal salts, it will be seen to be really still more so. Thus, upon reference to p. 340, we shall find, as the mean of experiments, that 1495·5845 grs. of the water, *plus* 267·785 grs. of NaO, CO_2, gave 627·4915 grs. of saline residue. Now subsequent experiment (p. 342) proved that this quantity of water must have contained of NH_3, 0·02678 gr., which is equivalent to 0·092963 gr. of $2\ NH_3,\ 3\ CO_2 + 2\ HO$. Consequently 627·584463 (627·491500 + 0·092963) — 267·785 (the weight of NaO, CO_2 employed) = 359·799463 grs. represent the true weight of the salt contained in that quantity of the water, which is equal to 24·05745 per cent.

TABLE

GIVING THE COMPOSITION PER GALLON OF THE WATERS OF THE DEAD SEA, AS SHOWN BY THE ANALYSES OF DIFFERENT CHEMISTS.

	MM. Lavoisier, Macquier, and Sage.	Dr. Marcet.	Prof. Klaproth.	M. Gay-Lussac.	Prof. Gmelin.	Dr. Apjohn.	Messrs. Herapath.
Specific gravity . . .	1·2403	1·2110	1·2450	1·2283	1·2120	1·1530	1·17205
Boiling-point . . .	undetermined.	undetermined.	undetermined.	undetermined.	undetermined.	221°	221°·75
Chloride of calcium . .	33·122·2115	3·221·2600	9·237·900	3·439·2400	2·726·8424	1·967·7098	2·014·2129
„ „ magnesium . .		8·561·7700	21·090·300	13·163·6911	9 988·5526	5·948·3270	6·417·6780
Bromide of magnesium . .	.. ..	.. ..	.. ..	.. ..	372·7022	162·2272	206·0708
Iodide of magnesium? . .	.. ..	.. ..	.. ..	.. ..	..	.. ..	very minute traces.
Chloride of potassium . .	.. ..	.. ..	.. ..	.. ..	1·420 0519	687·6492	998·7570
„ „ sodium . .	5·426·3125	9·050·0452	6·170·220	5·975·6795	6·004·7206	6 326·8569	9·935·2036
„ „ ammonium . .	.. ..	.. ..	.. ..	.. ..	6·1084	.. ..	4·9226
„ „ aluminum . .	.. ..	.. ..	.. ..	.. ..	76·0167	.. ..	45·8975
„ „ iron . . .	.. ..	.. ..	.. ..	.. ..	.. ..	.. ..	2·2304
„ „ manganese . .	.. ..	.. ..	.. ..	.. ..	179·6063	4·0355	4·9216
Organic matters . . .	.. ..	.. ..	.. ..	.. ..	.. ..	.. ..	50·6510
Nitric acid	.. ..	.. ..	.. ..	.. ..	.. ..	.. ..	doubtful traces
Carbonate of lime . . .	.. ..	.. ..	.. ..	.. ..	.. ..	.. ..	traces.
Sulphate of lime . . .	.. ..	45·77588	.. ..	.. ..	44·7107	60·5325	55·6800
Silica and bitumen . .	.. ..	.. ..	.. ..	.. ..	.. ..	.. ..	traces.
Fixed salts	38·548·5240	20·878·8510	36·498·420	22·578·6106	20·819·3118	15·157 3380	19·736·5254
Water	48 272·4760	63·891·1490	50·651·580	63·402·3894	64·020·6882	65·552·6620	62·306·9690
	86·821·0000	84·770·0000	87·150·000	85·981·0000	84 840 0000	80·710·0000	82·043·4944

XXXII.—*Analysis of the Well-Water at the Royal Mint, with some Remarks on the Waters of the London Wells.*

By William Thomas Brande, Esq., F.R.S., V.P.C.S. &c.

Previous to the year 1842, the Mint was supplied with water principally from two sources: the dwelling-houses, offices, and a part of the works, by the New River Company; and the steam engines, by wells partly supplied by so-called land-springs, and partly by a tunnel communicating with the Tower Moat; the principal supplies being derived from the latter; so that when in consequence of any works carrying on at the Tower, the access of the river to the moat was impeded, the operations of the Mint were not unfrequently obliged to be suspended; besides which, the water derived from that source was always muddy, and often very foul and offensive.

In consequence of this bad condition of the water in the Tower Moat, and the effluvia arising from it in hot weather, it was resolved in the year 1843, to drain and lay it dry. The Mint was accordingly altogether deprived of its supply of water from that source, and the land springs supplying the wells of the several steam engines, to say nothing of the impurity and hardness of the water thence derived, were found wholly inadequate to the wants of the engines. It therefore became necessary to have recourse to the New River Company for such additional supplies of water as might be wanted for carrying on the business of the Mint; and for this, their charges, as far as the steam engines were concerned, were at the rate of £10 per horse power *per annum;* but, from various causes, these supplies could not always be depended on, so that on several occasions a temporary suspension of the business of the Mint was the consequence of a deficient supply of water.

Under these circumstances it became my duty to suggest to the Master of the Mint, the adoption of such measures as might ensure for the future a regular and adequate supply of water for the use of the whole establishment, and to this end, it was necessary in the first instance, to make myself accurately acquainted with the actual condition of the several wells existing in the Mint, and with the quantity and quality of the water which might be derived from them. I was therefore authorised by the Master of the Mint to consult with Mr. Thomas Clark, an experienced Well Engineer, in reference to the subject; and I accordingly desired him to examine into the condition and capabilities, of all the wells, shafts, and tunnels, connected with the supplies of water throughout the building. This examination was carefully and effectually accomplished; and it appeared that the several wells were in a very dilapidated, and some of them, in a very dangerous state; that few of them were so situated, or conditioned, as to admit of being sufficiently or safely deepened, so as to yield an adequate supply of water; and that, as respected the wells in the several engine-houses, they were mere reservoirs connected with the tunnel-shaft from the Tower, and therefore almost exclusively supplied from the muddy source of the Tower Moat.

Having personally convinced myself of the correctness of this Report, and having had Mr. Clark's statement corroborated by Mr. George Rennie, I represented the matter in detail to the Master of the Mint, and suggested three plans for consideration, namely: 1. To derive the requisite supplies of water from the Water Companies. 2. To repair the present wells, and to deepen such of them as would admit of that operation. 3. To sink an entirely new well: and I strongly urged the adoption of the latter alternative, which, after due consideration, was agreed to. I therefore obtained proper plans and estimates from Mr. Clark, which, after having been submitted to the Board of Woods, and by their direction, to Major Jebb, were ultimately ordered to be carried into execution.

These plans included the sinking of an entirely new well; the erection of a capacious water-tank, at a sufficient height to supply the ordinary demands of the Mint; proper pumps for raising the water, and mains for distributing it over all parts of the buildings; together with fire-cocks, and other arrangements, the details of which would be irrelevant to the object of this communication.

It may be right to premise, that the total depth of this new well is about 426 feet; that the depth from the surface down to the chalk is about 224 feet; and the borings into the chalk about 202 feet; the following being the well-sinkers' account of the strata gone through; namely:

	Feet.
Made earth	11
Gravel and sand (with water)	13
Blue clay with a few sandy veins (no water) . . .	98
Coloured sand and pebbles (abundance of water) . .	14
Dark sand with veins of clay (little water) . . .	4

Mottled clay (dry)	6
Loamy sand and dark clay (little water)	5
Blue clay with shells	6
White rock (quite dry)	3
Green sandy rock and pebbles (dry)	3
Loamy green sand and black pebbles (little water)	5
Green sand and pebbles (abundance of water)	6
Dark sand with shells	40
Flints	10
Chalk	202
	426

The lining of the upper part of the well, through the gravel and nto the blue clay, is composed of stout cast iron cylinders, 1¼ inch thick, and 8 feet clear diameter; they are made in 5 feet lengths, with internal flanges 3 inches wide, packed, and jointed with strong bolts and nuts: these prevent all access of the land springs from above. The shaft is then steined to the depth of 88 feet, (that is, nearly through the blue clay), in 9-inch cemented brickwork; after which, cast iron cylinders are resumed, of 7 feet diameter, and these are continued down to the chalk; but after passing through the stratum of mottled clay, they include a series of cylinders of 6 feet diameter, the space between the outer and inner cylinders, being filled with gravel-pebbles; a bore-pipe, 20 inches diameter and 45 feet long, is then driven to about 10 feet into the chalk, and through this the boring is continued, by an 18-inch auger, to the entire depth of the well.

This well, and all the works connected with it, were completed at Christmas 1846, and on the 1st of January 1847, the whole of the works of the Mint, and the dwelling-houses, were supplied with the water, which is raised in a 6-inch main to a height of 50 feet above the surface, or 130 feet above the average level of the water in the well; and is delivered at the rate of 240 gallons per minute, by means of three pumps of 9-inch diameter and 8-inch stroke, into a tank supported upon a building of brickwork. This tank is 100 feet long, 30 wide, and 5 deep; it contains, therefore, 15,000 cubic feet of water, or 93,750 imperial gallons. Two 6-inch cast-iron mains, furnished with proper slide valves, descend from this tank, one passing on either side of the Mint, so as conveniently to supply the whole of the establishment: the daily consumption of water frequently exceeding 40,000 gallons; besides which, a daily supply of about 6,000 gallons is delivered, by means of a main laid from the Mint across Tower Hill, to the Tower, for the use of the inhabitants and the garrison; there being at present no serviceable wells in that fortress, and the water derived from the adjacent river being objectionable in point of cleanliness.

The average height which the water attains in the shaft of the Mint well is 80 feet from the surface. After a day's pumping it is lowered, upon an average, 20 feet, but there it remains stationary, the flow of water from below maintaining the level, or in other words, delivering at the rate of about 240 gallons per minute.

Before this well was completed, and before the boring into the chalk had been accomplished, the water derived from it contained 44 grains of dry saline matter in the imperial gallon. At present, the machinery being complete, and the well in full and daily use, the mean of several experiments in reference to the solid matter contained in the imperial gallon of the water, amounts to 37·5 grains.

The substances contained in each gallon of the water are as follow:

Sulphuric acid	7·44
Chlorine	6·31
Carbonic acid, (after boiling)	5·84
Silica	0·50
Sodium (combined with chlorine)	4·22
Soda, (combined with sulphuric and carbonic acids)	10·82
Lime	1·96
Magnesia	0·71
Organic matter Phosphoric acid Iron	traces.

The water evaporated to one-fifth of its bulk, and filtered, had lost almost every trace of lime and of magnesia, so that it is probable that the greater part of those substances were held in the state of *carbonates*, by excess of carbonic acid. The carbonate of lime forms films during boiling, which subside, and appear under the microscope in the form of very minute acicular crystals. The crystalline deposit obtained by slowly evaporating the water after the precipitated carbonate of lime has been separated by filtration, exhibits, under the microscope, three distinct forms; namely, cubes, (of chloride of sodium); prisms, which lie distinct upon the other salts, and are efflorescent, (sulphate of soda); and small aggregates of rhomboids intermixed with small spherical particles, like pin-heads, (carbonate of soda). The residue of the evaporation of the water, after having been gradually raised to a dull red heat, acquired a grey tint, and exhaled a slight odour of burning azotized matter; and a piece of moistened turmeric paper held in the evolved vapour was transitorily reddened.

I have not been able to detect any potassa in this water; and only a slight indication of the presence of a phosphate, in the precipitate deposited by the water during boiling.

Upon the whole, I am inclined to regard the following as a tolerably correct statement of the proximate saline components of this water:

	Grains in the imperial gallon.
Chloride of sodium	10·53
Sulphate of soda	13·14
Carbonate of soda	8·63
Carbonate of lime	3·50
Carbonate of magnesia	1·50
Silica	0·50
Organic matter Iron Phosphoric acid	traces.
	37·80

The specific gravity of the water at 55° is 10007. Its gaseous contents I have not ascertained.

A section of the well accompanies this paper, which will shew such details of its construction as I have not thought it necessary to enter into, as well as the relative thickness and position of the intersected strata.

I have examined the water of several other wells in and about London, some of which derive their supplies from the sands under the blue clay, and others, to a greater or less extent, also from borings into the chalk, and I think that in most cases, the latter waters are the more pure; that is, that in proportion as the borings are deepened into the chalk, the less are the solid contents of the water. There are in London and its vicinity, some very deep wells which yet do not reach the chalk; and others, of a less depth, which are carried into it: arising out of inequalities in the surface of the chalk, and the varying thickness of the blue clay itself; so that the variations in the relative quantity of solid matter in the waters derived from these wells, is no criterion of their respective depths.*

The *shallow wells* of the London district, by which I mean those which do not penetrate the blue clay, but derive their supplies from the gravels and sands above it, yield water of varying quality, but always much less pure than that of the deeper wells, and generally abounding in sulphate of lime, and consequently eminently *hard*, as respects the decomposition of soap, and other common culinary uses. There are many of these wells in which analysis detects indications of contamination by sewers, and by the vicinity of gas-pipes; and some of them have been disused and filled up on that account. There are also, as is well known, many which are either in churchyards, or upon their boundaries; and it is from these parish pumps, that the neighbourhood often exclusively derive their supply of drinking-water. I am at present examining the waters of several of these wells. In those which I have already examined, I have been struck with the abundance of *nitrates*, generally nitrate of lime; and this, in some of them is accompanied by what may be termed a large proportion of organic matter; so large indeed, that on proceeding in one case to heat the dry residue of the water to redness, a deflagration ensued; and yet, this water is bright and colourless, has no unpleasant taste, and is abundantly resorted to as very superior spring-water by a very populous neighbourhood.

How far such waters may or may not be salubrious, is not a question here to be discussed; but in some cases there can, I suppose, be no doubt upon the subject, inasmuch as I have found two of these waters of an evident, though slight, brown or peaty tinge, as furnished from the well; soon becoming brown on evaporation, and yielding abundant evidence of containing that species of humic extractive in which the adjacent soil no doubt abounds. I have in no instance been able to detect ammoniacal salts in any of these waters, but I presume that the nitric acid which they contain is the result of the oxidizement of ammonia.

It was my wish to have laid some of the results of these analyses more in detail, before the Society; my apology for such imperfect details is, the hope that they may engage the attention of other analysts; that the important subject of the condition of the waters of London and its vicinity may meet with the attention it deserves;

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* The chief peculiarity of these waters is derived from the presence of carbonate of soda, which notwithstanding the large relative proportion of other salts which they often contain, confers upon them a peculiar *softness* as regards the *soap-test*, and seems to render them well adapted for domestic use, and especially for the infusion of tea and coffee.

and that the comprehensive subject of the metropolitan supply of water may be scientifically, and accurately, and dispassionately considered, by those who are adequate to the task.

As regards the leading question of River supplies on the one hand, and Artesian supplies on the other, I cannot however, help expressing myself decidedly in favour of the former. Deep wells are pre-eminently valuable for local uses; but, the peculiarities of the waters which they afford; the depth from which, in many situations and under most circumstances, those waters must be raised; the possibility, and I think I may say, probability of the inadequacy of their supply; and the chances of their mutual interference, are some of the circumstances which in my mind should be well weighed, before the gigantic scheme of the supply of the metropolis from such sources is seriously entertained. On the other hand, pure River-water is already upon the surface, in various quarters, in unlimited quantity, and at no great distance; and when filtered, an operation which, as experience has shewn, is attainable to any extent, its quality is in all respects superior. That many parts of London are badly and inefficiently supplied with water, and that in some places none is laid on, cannot be denied; but a slight movement in a proper direction, would I think remedy all real evils under this head. I must further beg leave to express my opinion in favour of the adequacy of the existing Water Companies to the accomplishment of all that can be reasonably required: the magnitude of their united means, the general excellence of their arrangements, the practical skill with which they have been devised and executed, and the resources which are still open to them where increase of supply is demanded, are the circumstances upon which I found this opinion.

I shall conclude with a short comparative table, showing the relative quantity of solid matter contained in such river and spring waters as have been carefully analysed; intending, upon a future occasion, to extend the list, to give the details of the analyses, and the names of the analysts; in their present imperfect state, however, the following details will serve to illustrate some of the points touched upon in the preceding notice. The wells which are termed *deep*, derive their water from the strata below the blue clay, and some of them penetrate into the chalk; those termed *shallow*, are supplied from the strata above the blue clay. This is the case with most of the common London wells, which, however, are often steined to a considerable depth in the clay, for the purpose of forming a reservoir.

		Solid matter in the imperial gallon.
Thames at Greenwich		27·9
„ London		28·0
„ Westminster		24·4
„ Brentford		19·2
„ Twickenham		22·4
„ Teddington		17·4
Average of the Thames between Teddington and Greenwich		23·2
New River		19·2
Colne		21·3
Lea		23·7
Ravensborne at Deptford		20·0
Combe and Delafield's Brewery, Long Acre.	Deep well	56.8
Apothecaries Hall, Blackfriars	ditto.	45·0
Notting Hill	ditto.	60·6
Royal Mint	ditto.	37·8
Hampstead Waterworks	ditto.	40·0
Berkeley Square	ditto.	60·0
Tilbury Fort	ditto.	75·0
Goding's Brewery, (Lambeth)	ditto.	50·0
Ditto	shallow well	110·0
More's Brewery (Old Street)	deep well	38·0
Ditto	shallow well	110·0
Trafalgar Square Fountains	deep well	68·9
Well in St. Paul's Churchyard		75·0
„ Breams Buildings		115·0
„ St. Giles, Holborn		105·0
„ St. Martin's, Charing Cross		95·0
„ Postern Row, Tower		88·0
Artesian well at Grenelle, near Paris		9·86

XXXIII.—*On Titanium.*

By Professor Wöhler.

The beautiful copper-coloured cubic crystals of titanium, the formation of which have been so often observed in the blast iron-furnaces, are not that which we have hitherto considered them; they are not a simple, but a compound body. They consist of a combination of cyanide of titanium with nitride of titanium, composed according to the formula: $Ti\,C_2\,N + 3\,Ti_3\,N$, and contain in 100 parts, titanium 78·00, nitrogen 18·11, carbon 3·89; that is, they consist of cyanide of titanium 16·21, nitride of titanium 83·72.

The treatise laid before the Göttingen Society contains the details of the manipulation used in the analysis and the proofs for assuming this composition; here the author only communicates the behaviour which led to the detection of the carbon and nitrogen. When these cubic crystals are heated in dry chlorine gas, liquid chloride of titanium is produced; at the same time a crystalline, volatile, yellow substance sublimes in considerable quantity. This substance is a compound of chloride of titanium with chloride of cyanogen, which can be directly and easily produced from the two chlorides. At the end of the operation, about 1 per cent of residue remains behind, consisting of graphite in fine scales; this is, however, an accidental impurity, and exact experiments have shown that this graphite plays no part whatever in the formation of the cyanogen. When these crystals are powdered, mixed with hydrate of potash and fused, ammonia is evolved and titanate of potash is formed.

When the crystals are heated to redness in a porcelain tube, and the vapour of water in a continuous stream is passed over them, a considerable quantity of hydrogen gas is set free, as observed by Regnault; but there is also at the same time a disengagement of ammonia and hydrocyanic acid. If this experiment be made with the crystals in their natural state (not powdered), the titanic acid produced maintains the form of rounded cubes; but under a magnifying power of 300 diameters they have the appearance of an aggregate of crystals, the greater part of which present themselves in an entire form; and what is most remarkable, this form is identical with that of the mineral *Anatase*, that is, they are pointed octahedrons, with a square base, possessing a strong lustre, and all the peculiarities belonging to this mineral.

The cubes, when reduced to powder, have, moreover, the remarkable property, if mixed with oxide of copper, lead, or mercury, and heated, of emitting a lively sparkling flame, and reducing the oxides of these metals; this behaviour was taken advantage of for determining the proportion of carbon in them; the heat evolved is so intense and instantaneous, that even copper runs into a globule in the glass tube. With regard to the formation of the crystals in the smelting furnace, the writer believes there can be no doubt that it stands in intimate connection with the formation of cyanide of potassium, which has been so often observed in these furnaces; some experiments which he undertook to make this, if possible, more clear, fully confirm the supposition. A mixture of ferrocyanide of potassium and titanic acid was exposed in a well-closed crucible, for an hour, to a heat in which nickel would melt; the result was a brown unfused mass, which under a magnifying power of 300 diameters, presented, besides the particles of metallic iron, throughout the whole mass, a network of copper-coloured, strongly metallic, shining, short prisms, which, as indicated by the colour, are composed of the same substance as the cubic crystals. After removing the iron by means of hydrochloric acid, these remained, mixed with carbon, and exhibited all the properties belonging to the cubic crystals.

The titanium used in all these experiments was produced at the Ruebeland smelting-furnace, in the Hartz, where lately a mass of titanium has been found, estimated at 80 lbs. (Hanover) weight. The Author has not had an opportunity of examining the crystals from other furnaces, but there can be scarcely a doubt that all are perfectly identical in composition.

Nitride of Titanium.—As long as the cubic crystals of titanium were considered to be pure titanium, it was, from their similarity of colour, a pardonable fault to regard as the true metal the copper-coloured substance first produced by H. Rose from the double chloride of titanium and ammonium, by subjecting the same to the action of heat in gaseous ammonia. But this latter substance is likewise not that which we believed it to be, but a nitride of titanium, composed according to the formula $Ti_3\,N_2$, or more probably $Ti_6\,N_4$, that is $3\,Ti\,N + Ti_3\,N$, and contains nearly 28 per cent of nitrogen; also, on more accurate comparison, a difference in the colour may be perceived; this latter compound being much redder than the cubic crystals, which have a tint of yellow; 100 parts gave by combustion only 120, whereas if pure titanium, they should yield 166 parts. When fused with hydrate of potash, gaseous ammonia was abundantly evolved.

This is not the only isolated combination of titanium and nitrogen that can be produced; the Author has found, that two other compounds exist. All these compounds exhibit the same remarkable phenomena as the cubic crystals (viz. under a lively evolution of flame they are oxidized, and the metallic oxides reduced) when powdered and mixed with the oxides of the easily reducible metals and subjected to the influence of heat. All these compounds can sustain a temperature at least equal to that in which silver would melt without undergoing decomposition. All give, when fused with hydrate of potash, gaseous ammonia. The nitride of titanium, $Ti\,N$, is produced when titanic acid is subjected to a strong heat in a stream of gaseous ammonia; its powder is of a dark violet colour, with a copper-coloured tint; in small pieces it possesses a violet copper colour, and metallic lustre.

The nitride of titanium, $Ti_5\,N_3$, or more probably $2\,Ti\,N + T_3\,N$, is produced when Rose's titanium is submitted to the action of a stream of hydrogen at a strong red heat, whereby the nitrogen which it gives off is carried away in the form of ammonia; it possesses a metallic lustre, and a brassy or almost gold-yellow colour. This compound is obtained, (impregnated, however, with carbon), when titanic acid is heated to redness in a stream of cyanogen gas, or in the vapour of hydrocyanic acid; here, however, it must be remarked, that cyanide of titanium is not formed.

The Author can also reply to the question—What is the character of pure titanium? This substance was first observed by Berzelius; it was not, however, closely examined by him; it is that body which is produced by heating the double fluoride of potassium and titanium with potassium. The Author prepared it in a covered platinum crucible; the reduction was accompanied by a lively evolution of flame. After washing and separation by water, pure titanium remains behind, as a dark green, uncrystalline, and tolerably heavy powder. Even after being subjected to pressure, one cannot discern a shade of colour approaching that of copper, and under the microscope it appeared as a cemented mass, having the colour and lustre of iron. If heated in contact with the air, it burns with much splendour; sprinkled into a flame, it burns at a considerable distance above its point with the same brilliancy and splendour as uranium; if brought to a red heat in oxygen gas, it is suddenly consumed with a splendour resembling a discharge of the electric fluid. Its comportment in chlorine gas is very similar, requiring also, however, the aid of heat; mixed with minium and heated, it burns with such an intense evolution of caloric, that the mass is thrown out with a report. Titanium possesses the property of decomposing water; at the temperature of 100° C. (212° F.) in pure water, hydrogen gas begins to be evolved, and in warm hydrochloric acid it is dissolved, with a brisk disengagement of hydrogen. Ammonia throws down from the solution a black oxide; if the liquid be then warmed, a disengagement of hydrogen takes place, the precipitate becomes first blue and is afterwards transformed into white titanic acid.

The Author has the intention of extending his experiments on the compounds of nitrogen to the other substances nearly allied to titanium, namely to silicium and boron, in the hope of increasing our knowledge respecting the nitrides of the metals, for the discovery of which we have to thank Schroetter, and also in the hope of obtaining something definite from the compounds discovered by Balmain.

NOTICES

OF

PAPERS CONTAINED IN THE FOREIGN JOURNALS.

*On the isomeric modifications of phosphoric acid.**—Rose has shewn that the oxides of tin, and the other metallic oxides which possess an acid character, are capable of assuming very different properties when exposed to different degrees of temperature, but phosphoric acid far surpasses any of these metallic acids in the paradoxical isomeric modifications which it undergoes.

1. *Metaphosphoric acid.*—The metaphosphoric acid of Graham exists in no less than three isomeric modifications, the one of which is that originally described by its discoverer, and is prepared in combination with soda by melting and allowing to cool slowly the acid phosphate of soda, or microcosmic salt. The solution of this salt is neutral, or very slightly acid, and is characterized more particularly by producing precipitates with neutral solutions of many salts of the earths and metallic oxides, which are generally soluble in an excess of the soda salt, and possess the remarkable property of conglomerating, when shaken, into a heavy thick oily mass. The solution of the salt itself affords no precipitate with a diluted and filtered solution of white of egg, but a precipitate is immediately formed in the mixture on the addition of acetic acid. The properties of this solution with reference to other salts, have been carefully investigated by Rose, who finds that the acid separated from the soda salt by precipitation with silver and subsequent treatment of the silver salt with sulphuretted hydrogen, differs in some respects from the metaphosphoric acid obtained by burning phosphorus in oxygen gas.

The acid separated from the soda salt, produces no immediate precipitate in chloride of barium, a flocculent sediment being deposited only after the expiration of some time, baryta water, on the other hand, even when not in excess and the liquid is still acid, produces a precipitate directly. With the metaphosphoric acid obtained by the combustion of phosphorus, an immediate copious precipitate is produced by chloride of barium, which requires a large excess of the acid to dissolve it.

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* Pogg. Ann. LXXVI. 1.

The oily resinous precipitate produced by the acid of Graham's salt in nitrate of silver, has been analysed by Weber, and found to contain quantities corresponding to the formula $3\ AgO, 2\ PO_5 + HO$. This composition accounts in some measure for the acid obtained from the salt possessing different properties from that produced directly from phosphorus. When, however, the silver precipitate is separated at once from the liquid, and dried between blotting paper, its composition then corresponds to that of the soda salt.

2. The second modification of metaphosphoric acid is that contained in the singular class of salts prepared by Fleitmann and Henneberg, by cooling very slowly melted microcosmic salt. The salt of soda thus prepared, has precisely the same composition as Graham's salt, but differs from it in being opaque, and of a crystalline structure, while the latter is transparent and amorphous. It crystallizes from solution with four atoms of water, and the solution, like that of Graham's salt, has a neutral reaction.

The most remarkable property of this modification of the acid, is that of producing soluble compounds with all bases, and this enables it to be easily distinguished from all others.

3. The acid in the salts, formerly known as acid phosphates, which are insoluble in water and in acids, may be viewed as the third submodification of metaphosphoric acid. These salts are obtained by the fusion of salts with phosphoric acid, until a portion of the fused mass precipitates a solution of white of egg.

All these modifications of the acid, have the same capacity of saturation; they all precipitate a solution of albumen, which is an excellent qualitative test for a metaphosphate; it is necessary, however, to add acetic acid to the soluble salts, in order to effect this precipitation.

The property of precipitating chloride of barium is peculiar to that modification of the acid, which is produced by the combustion of phosphorus.

When ordinary phosphoric acid is heated for several hours without volatilization occurring, the modification well known as pyrophosphoric acid is obtained; if, however, the heat be continued until the acid begins to volatilize, the product then affords a copious precipitate with albumen and chloride of barium; nitrate of silver is also precipitated white, which precipitate becomes resinous when agitated, this proves that metaphosphoric acid has been produced. Uncertainty still reigns respecting the true composition of melted phosphoric acid. Rose found in three experiments in which the acid was successively heated to higher temperatures, that the amount of water contained in the product was less each time than is required by the formula $PO_5 + HO$. This result appears to indicate that by constantly applied heat, the whole of the water might be removed, and anhydrous phosphoric acid obtained.

Rose is inclined to explain the various properties of metaphosphoric acid, by assuming that it is a conjugate acid. The conjunct, he states, might be anhydrous phosphoric acid, associated in varying proportions with pyrophosphoric, or ordinary phosphoric acid, and it may be this conjunct, or the anhydrous acid which possesses the property of precipitating albumen, and communicates this property to all the modifications of metaphosphoric acid.

2. *Pyrophosphoric acid.*—This modification of phosphoric acid, requires the assumption of at least two sub-modifications to explain the different characters of its salts. The one acid is contained in the salt obtained by heating ordinary phosphate of soda to redness, and in the salts derived from it. The other is produced in a similar manner to the insoluble metaphosphates of Maddrell, when salts containing an excess of phosphoric acid are heated to a temperature somewhat lower than that which is required to convert them into metaphosphates. By this processs a copper salt at least is produced, by treating nitrate of copper with phosphoric acid, which is quite as insoluble as metaphosphate of copper. The acid of this salt is, however, easily eliminated by sulphuretted hydrogen, and has in the aqueous solution, the same properties as ordinary pyrophosphoric acid. Rose accounts for the different properties and saturating powers of pyrophosphoric and ordinary phosphoric acids, by the isomerism of the two acids, and considers it not improbable that the one atom of water in ordinary phosphate of soda, might be expelled without converting the salt into a pyrophosphate. Experiments undertaken with this object in view have not, however, proved successful.

Pyrophosphoric acid has a strong tendency to form double salts, as has been pointed out by Stromeyer and more recently by Persoz, and Baer has lately made the interesting observation, that the precipitates produced by a solution of pyrophosphate of soda which are insoluble in an excess of the precipitant, are often insoluble double salts of the soda salt with the pyrophosphate produced, in which the soda and the other base can mutually replace each other, without both, as it appears, being contained in the double salt in a definite simple relation. Even the silver salt contains small portions of soda.

Rose describes the reactions of the pyrophosphates and of the isolated acid, with great minuteness, and establishes the fact in contradiction to the statements of Berzelius, that pyrophosphoric acid does not precipitate albumen, and that this is the chief and most characteristic mode of distinguishing this acid from metaphosphoric acid.

3. *Ordinary phosphoric acid.*—Rose calls attention to one property of the salts of this acid which appears to have been overlooked, and which is very characteristic of them, it is the solubility of very many insoluble phosphates in an excess of the saline solution from which they have been precipitated by phosphate of soda. This solution generally possesses the property of affording a copious precipitate when heated, which disappears on cooling. Double salts are, therefore, produced, which are decomposed

by a high temperature. Precipitates produced by a pyrophosphate, are also often soluble in an excess of the saline solution; these solutions when heated also become turbid, but the turbidity is permanent even when the solution cools.

The reactions of phosphate of soda with the whole series of metallic salts, have been again minutely investigated in the paper before us; for the detail of these experiments we must refer to the original. One excellent test for the presence of phosphoric acid, recently proposed by Svanberg and Struve, claims, however, particular attention: this is molybdate of ammonia. The test is so delicate, that the most minute traces of the acid are detected by it under circumstances when other tests are inapplicable.

If a solution of molybdate of ammonia is added to any solution of a phosphate, and then a sufficient quantity of hydrochloric, or better of nitric acid to dissolve the precipitate which is at first formed, the liquid immediately becomes coloured yellow, and deposits a yellow precipitate of molybdic acid, which, however, is not the ordinary modification of the acid, and is only produced in the presence of phosphoric acid.

If the phosphate for examination is insoluble in water, a solution in nitric acid may be employed for this test. Heat accelerates the precipitation. The yellow precipitate is soluble in ammonia, as well as in an excess of the phosphate. For this reason the test is peculiarly applicable for detecting small quantities of phosphoric acid, and larger quantities of phosphate are liable to elude detection from the great amount of molybdate required to produce the yellow precipitate after supersaturating by means of nitric acid.

The colour of the solution does not interfere with the distinct recognition of the characteristic colour of the precipitate. It is only the salts of ordinary phosphoric acid which are subject to this reaction, the other modifications must be brought into that state therefore, before the test can be applied.

On a series of insoluble alkaline salts of phosphoric and arsenic acids.[*]—The only known double salt of phosphoric acid, with an earth and an alkali, which is insoluble in water, is the phosphate of ammonia and magnesia, and this contains two atoms of magnesia to one of ammonia. Rose, however, has discovered that similar double salts of potash and soda, as well as of lithia, can be produced both with magnesia and with lime.

The circumstances under which these salts are most readily prepared, are:

When an atom of pyrophosphate of the earth is intimately mixed with an atom of carbonated alkali, and the mixture heated to redness, until it suffers no further loss of weight. The mass in this operation is not melted, nor even agglutinated. It is then heated with water for some time, and washed with hot water. It is requisite that these proportions be adhered to, in order to secure the formation of a considerable portion of the salts.

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[*] Pogg. Ann. LXXVII. 288.

The compounds obtained, yielded, with few exceptions due to subsequent decomposition, results, on analysis, which indicated very closely two atoms of the earth to one of alkali and one of phosphoric acid. The washing process requires some time, but the alkali may often be entirely removed if it be too often repeated, and its place in the compound is then filled by water. The following compounds have been obtained in this manner, and were analysed by M. Weber.

Phosphate of potash and lime, phosphate of soda and lime, phosphate of potash and strontian, phosphate of soda and strontian, the composition of this, however, approached nearer to the formula:

$$2\ (NaO,\ 2\ StO,\ PO\ ) + HO,\ 2\ StO,\ PO\ .$$

phosphate of potash and baryta. The phosphates of potash and baryta, and of soda, and baryta did not agree closely with the formulæ.

Phosphate of potash and magnesia.

Phosphate of soda and magnesia.

Phosphate of lithia and lime.

Chlorides of the alkalies yield the same salts, when fused with phosphates of the earths.

If, however, phosphates of the earths are contained in acid solutions, in common with the alkalies, the former can then be precipitated by ammonia, and the precipitate contains no alkali. The compounds described above are, therefore, not produced in the humid way, although the total amount of the phosphate is not precipitated in consequence of the presence of the ammoniacal salt that is produced.

Other double salts which are soluble, and contain two atoms of alkali to one of an earth and one of phosphoric acid, appear also to be formed under certain circumstances.

When an organic substance is charred, and the charred mass is extracted with water, the aqueous solution frequently contains phosphates of the earths, particularly phosphate of lime, which are separated by evaporation to dryness, and treatment of the dry residue with water. The pyrophosphates of the earths, have in this case been dissolved by phosphates of the alkalies, with which they form double salts.

When an excess of pyrophosphate of soda is heated to incipient redness with carbonate of lime, the aqueous solution of the fused mass contains phosphate of lime. In performing this experiment, two atoms of pyrophosphate of soda should be employed to one atom of carbonate of lime. The lime is detected in the solution by oxalic acid. The phosphate of lime is not easily separated by evaporating the solution to dryness, or by passing carbonic acid through it, but readily when carbonate of soda is added, the whole being then evaporated to dryness. The phosphate of lime thus precipitated contains, when washed, no carbonate of lime. A double salt has obviously been formed, in this case, of phosphate of soda and phosphate of lime; the latter separates when a portion of the soda in the solution is converted into carbonate of soda.

The arseniates of the earths are even more completely decomposed by fusion with carbonates of the alkalies than the phosphates. The double compounds formed, were those of potash and soda, with magnesia and arsenic acid; they are easily decomposed, however, by water, that substance in part replacing the alkali.

*On the products of the distillation of lactic acid, and of lactate of copper, by Engelhardt.**—When highly concentrated lactic acid is exposed in a retort to a temperature of from 130—140° (298° to 316° F.) an acid, watery liquid distils over, possessing a somewhat empyreumatic odour. This liquid is dilute lactic acid. If the temperature be kept up in the retort, until no more water passes off, a residue is obtained which is amorphous, of a brown red colour, melts at a temperature below the boiling point of water, possesses a very bitter taste and is soluble in alcohol, this residue consists of anhydrous lactic acid ($C_{12} H_{10} O_{10}$). This acid is very slightly soluble in hot water, and is deposited almost entirely when the water cools—it is precipitated from alcohol by water. Boiled with water for a length of time, or exposed for a long period to a moist atmosphere, the anhydrous acid is again converted into the ordinary modification. This transformation is more speedily effected by the alkalies and alkaline earths.

Heated above 250° (482° F.) anhydrous lactic acid evolves carbonic oxide gas, which towards the end of the operation, if the temperature has not risen above 260° (500° F.) is mixed with only 3 to 4 volumes per cent of carbonic acid. During this process of distillation a yellow liquid condenses in the cooled receiver, which either deposits crystals or solidifies into a crystalline magma, a small quantity of a light porous charcoal remaining in the retort. The condensed product was found to be a mixture of aldehyde, lactide, citraconic and hydrated lactic acids.

Lactone and acetone which had been previously found in the distillate by Pelouze, were not obtained by Engelhardt. The other products appear to result from the decomposition of lactide, which the author was unable to obtain from anhydrous lactic acid without a partial decomposition.

In one experiment in which 19·5 grms. of anhydrous lactic acid were decomposed at a temperature of 260°, (500° F.) and which operation lasted eight hours, 12·2 per cent of aldehyde, and 14·9 per cent of lactide were obtained, while 1 per cent of charcoal remained in the retort. At a higher temperature, e. g. 300° C. (572° F.) the evolution of gas is much more copious, and the quantity of aldehyde is increased, the lactide being then decomposed into aldehyde and carbonic oxide, as is shown by the following formulæ :

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* Ann. der Chem. u. Pharm. LXX. 241.

1 eq. Aldehyde	$C_4 H O_2$
2 ,, Carbonic oxide . . .	$C_2 O_2$
1 ,, Lactide	$C_6 H_4 O_4$

The products of decomposition of anhydrous lactate of copper, vary likewise with the temperature employed. Between 200 and 210° (292° and 410° F.) carbonic acid is evolved, and aldehyde with some hydrated lactic acid collected in the receiver, (the latter being probably due to some water of crystallization in the lactate). The oxygen in the oxide of copper has here evidently converted the carbonic oxide into carbonic acid. The evolution which was copious at a temperature of 210° (410° F.) gradually ceases, and metallic copper, and anhydrous lactic acid remain in the retort, which latter is decomposed when the temperature has risen to 250 or 260° (482° to 500° F.).

The author recommends the preparation of aldehyde from the lactates containing a weak base. The decomposition of the lactates containing strong bases, gives rise to very different products, an account of which is reserved for a future occasion.

*Allantoin in the urine of the calf.**—It is well known that the allantoic fluid of the cow, contains a peculiar body, allantoin. This fluid is also known to be the urine of the fœtus. Wöhler suspected, and has proved that the urine of the living newly-born calf, also contains this substance as a constant and physiologically essential ingredient. The urine of the calf may be employed as a source of allantoin, several grammes of which being contained in or procurable from a single well filled bladder. The urine is evaporated to the consistence of a thin syrup, without being allowed to boil, and is then left standing for several days, when allantoin crystallizes from it, mixed with much phosphate of magnesia, and an amorphous gelatinous body, consisting chiefly of urate of magnesia. The urine is diluted with water, and poured off with the gelatinous matter from the crystals. These are then washed once or twice with cold water, and heated with water to the boiling point, when they dissolve, leaving the insoluble phosphate of magnesia. The solution is rendered colourless by animal charcoal. The hot filtered solution should then be acidulated with a few drops of hydrochloric acid to prevent the precipitation of a little phosphate of magnesia which may have dissolved, allantoin then crystallizes perfectly colourless from the cold liquid.

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* Ann. der Chem. und Pharm. LXX. 229.

The crystalline form of allantoin, prepared by the foregoing method, is always different from that obtained from the allantoic fluid, and from uric acid, however often it may have been recrystallized. The crystals are thinner, and grow together in bundles, while those from the latter sources are well defined, particularly at their terminations. This modification of form appears to arise from a very slight admixture of some foreign substance, which is in too minute quantity sensibly to affect the composition of the allantoin, and which is perfectly separated by combining it with silver, and subsequently decomposing the silver compound by hydrochloric acid.

*On the composition of Stearin by G. Arzbächer.**—The discordant results obtained by different analysts, with reference to the composition of stearin, (*see* Gmelin, Handbuch, Bd. IV. Seite 200), induced the author to reinvestigate the composition of this fat. The results of his investigation prove that the stearin of ox suet and mutton suet, are two distinct compounds. The analysis of Chevreul and Lecanu having reference to that from the ox, while those of Liebig and Pelouze, apply to the fat of the sheep. The mean of four analyses of stearine from three different sources yielded the following results:

	Carbon.	Hydrogen.	Oxygen.
Stearin from ox suet	78·74	12·27	8·99
Stearin from mutton suet . .	76·50	12·28	11·22

The former would, therefore, consist of 1 atom of glycerin + 2 atoms of stearic acid — 8 atoms of water, while the latter is composed of 1 atom glycerin + 2 atoms of stearic acid — 4 atoms of water.

Their formulæ being respectively:

Stearin of the ox . . . . $C_{142}\ H_{134}\ O_{12}$
„ „ sheep . . . . $C_{142}\ H_{138}\ O_{16}$

100 parts would, therefore, yield by saponification:

	Ox tallow.	Mutton tallow.
Stearic acid	98·15	94·90
Glycerin	8·50	8·23
	106·65	103·13

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* Ann. der Chem. und Pharm. LXX. 239.

Experiments with albumen, casein and fibrin, by F. Bopp.[*]—Albumen, casein, and fibrin were exposed by the author to the same chemical agents, with a view to ascertain whether the products were the same in the case of each. Acids, strong alkali, and putrefaction, gave rise in every case to the formation of leucin; alkali and putrefaction, again destroyed this product, when their action was prolonged for a sufficient length of time, giving rise to a large quantity of valerianic acid.

Acids and alkali give rise to the formation of tyrosin; the alkali if allowed to exert its influence sufficiently long, again decomposes this substance. Putrefaction, however, which extends its influence beyond the stage at which leucin is produced, stops short before the formation of tyrosin is effected.

Besides the well characterized substances, leucin and tyrosin, another crystallizable substance was obtained by the action of acids, but was not more minutely examined by the author. In like manner a volatile crystalline body was observed as resulting from the putrefactive process, characterized by a penetrating odour, and an oily acid, but slightly soluble in cold, but more soluble in hot water, the lead salt of which is resinous and soluble in alcohol.

Leucin is the first product of the action of hydrate of potash on any of these bodies; tyrosin is an after-product. The acid, therefore, is the producer of the tyrosin, and carries on a similar action to a greater extent than the process of putrefaction, giving rise, however, at the same time to a smeary nitrogenous substance, which was not observed as the result of the putrefactive process. The action of the acids is not attended by the evolution of any gases, while putrefaction gives rise to abundance of carbonic acid, sulphuretted hydrogen and water, which are the simplest constituents or proximate principles of these complex groups of atoms. Nitrogen appears in five different products of these decompositions, in ammonia, leucin, tyrosin; a substance similar to these two latter observed in small quantity, and in the volatile body so characteristic by its intense odour. The sulphur of these protein compounds is evolved as sulphuretted hydrogen when putrefaction or alkali are the destructive agents; when acids are employed to effect the decomposition, it remains in combination with a brown amorphous mass not yet further investigated.

On the chemical composition of bones.[†]—The composition of the phosphate of lime contained in bones, has generally been assumed upon the authority of Berzelius to be represented by the formula 8 CaO, 3 PO_5. Some chemists, however, e. g. Marchand and Boussingault, have expressed an opinion that the true composition of this compound should be expressed by the formula $3\,CaO, PO_5$. With a view to clear up these contradictory statements, Heintz has most thoroughly reinvestigated the entire composition of the bones of man, of the ox, and sheep.

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[*] Annalen der Chem. u. Pharm. LXIX. 16.

[†] Pogg. Ann. LXXVII. 267.

The following tabular statement contains the numerical results of his analyses.

Of the two analyses of human bone, the first was executed with bone which had been charred, while for the second, the inorganic constituents were extracted from the dried bone by muriatic acid, in order to avoid any possibility of error, which might possibly have arisen from a loss in phosphoric acid, in the process of charring. The two experiments prove that the temperature employed in the case of the first was not sufficiently high to cause any decomposition of the phosphates.

The carbonic acid has been calculated as in combination with lime, and the magnesia as in combination with phosphoric acid.

	Ox.	Sheep.	Man.	
			I.	II.
Carbonate of lime . .	7·07	7·00	6·36	6·39
Phosphate of magnesia ($3\,CaO\,PO_5$) . . .	2·09	1·59	1·23	1·21
Phosphate of lime ($3\,CaO\,PO_5$)	58·30	62·70	60·13	59·67
Lime	1·96	2·17	1·81	1·62
Organic matter, &c. .	30·58	26·54	30·47	31·11
	100	100	100	100

The excess of lime indicated by these analyses was found by direct experiment to be in combination with fluorine.

The composition of bones, therefore, irrespective of the organic matter would be:

	Ox bone.	Sheep bone.	Human bone.	
			I.	II.
Carbonate of lime . .	10·07	9·42	9·06	9·19
Phosphate of magnesia ($3\,MgO, PO_5$) . . .	2·98	2·15	1·75	1·74
Phosphate of lime ($3\,CaO\,PO_5$)	83·07	84·39	85·62	85·83
Fluoride of calcium . .	3·88	4·05	3·57	3·24
	100·00	100·00	100·00	100·00

These experiments therefore prove:

1. That the bones of the vertebrate animals, contain a small amount of fluoride of calcium, as has been already shewn by Berzelius, Frerichs, Erdmann and others.

2. That the chief mass of the bones which communicates solidity to their structure, is entirely free from chlorides, from sulphates, and from iron. Wherever these have been found as constituents of bone, the fluids contained in the bone had not been previously removed by water.

3. That the amount of fixed bases in bones is exactly sufficient to saturate the acids associated with them, and consequently not only the phosphate of magnesia, which is only difficultly soluble, when it contains three atoms of base to one of acid, and in which state it can only be contained in bone that has been treated with water, but also the phosphate of lime must be contained in such proportion as to correspond to the formula $3\,RO, PO_5$.

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